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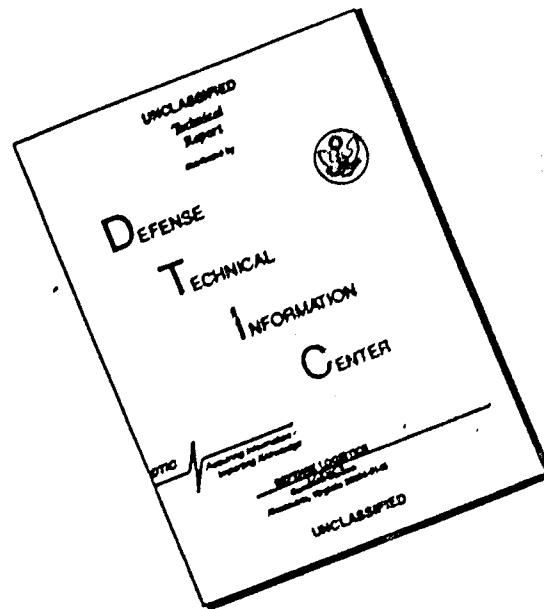


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*Air Products and Chemicals*

111106

*Research and Development Department*

SSD-TDR-62-8

STUDY OF LIQUID OXYGEN

CONTAMINATION

Final Report

by

R. H. Foster

AIR PRODUCTS and CHEMICALS, Inc.  
Allentown, Pennsylvania

A. P. I. Research Project Nos. 03-9-2880, -1, -2

Contract No. AF 33(616)-6730

Project No. 3148

Task No. 30196

May 1961

Directorate of Rocket Propulsion  
AIR FORCE FLIGHT TEST CENTER  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
Edwards Air Force Base, California

Copy No. 20

FOREWORD

This project was carried out at the Research and Development Facility of Air Products and Chemicals, Inc., Emmaus, Pa., Dr. Clyde McKinley, Director, under Air Force Contract AF 33 (616)-6730, Project No. 3148, Tank No. 30196.

The work was performed under the direct supervision of B. M. Bailey from July 1959 until September 1960, C. J. Sterner until February 1961, and R. H. Foster until completion of the project in May 1961. The following people contributed actively to the program:

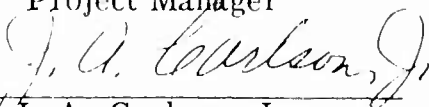
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The contract was let by the Wright Air Development Center, Wright Patterson AFB, Ohio, being initiated by Forrest S. Forbes, WCLPPFR. Mr. Forbes was the first engineering monitor (WCLP). He was succeeded in the early part of 1960 by Mr. Hugh E. Malone (then FTRPC, now DGPC) when the monitoring agency was changed to the Directorate of Rocket Propulsion, Edwards AFB, California.

Report Approved

  
R. H. Foster

Project Manager

  
J. A. Carlson, Jr.

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Director, Research and  
Development

ABSTRACT

This Final Report summarizes the work performed in accordance with contract AF 33(616)-6730. The purpose of this study was to develop a better understanding of the physical, chemical and mechanical relationships involved in developing realistic parameters for specification purposes for the application of oxygen to missiles. The significant sources and degree of contamination are supplied as a background survey and the current specifications for liquid oxygen and ground support equipment are discussed. Recommendations for liquid oxygen specifications and for equipment operation are presented. Sources and mechanisms for ignition of Liquid Oxygen systems, factors related to solid contaminants, cleaning and purification of oxygen equipment and handling systems have been included. Also as part of this contract, the contractor developed safety standards for use in high pressure oxygen and helium gases for later incorporation in the Liquid Propellant Safety Manual published by the Liquid Propellant Information Agency. As part of this program, a three-month analytical survey was made at Cape Canaveral and summarized herein.

A bibliography and Appendixes are attached.

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## I. INTRODUCTION

Over the past several years, several groups and agencies associated with rocket propulsion have been concerned with the quality of liquid oxygen required to insure reliable performance. The work of these groups has resulted in several sets of recommendations and specifications, each of which reflects the opinions and viewpoints associated with the group's specific problems. This present program was established to provide assistance in resolving the different viewpoints and to present current information and guidance to users of liquid oxygen and designers of liquid oxygen handling systems.

In July 1959, Air Products and Chemicals, Inc. was awarded a study contract to investigate the significance of contaminants of liquid oxygen, the sources and degree of contamination, and on the basis of these findings, to establish design criteria and recommended procurement and use limit specifications for the missile liquid oxygen. This study involved a background survey intended to identify the various soluble and insoluble contaminants which are found in liquid oxygen, and their compatibility with liquid oxygen and with each other under the environments which are encountered in liquid oxygen systems.

Sources of contamination and factors relating to prevention of occurrence, solubility of each contaminant in oxygen, lower explosive limits for flammable contaminants, and general important physical and useful constants of oxygen in all contaminants as related to each other were to be investigated. These data were to be correlated and used to determine practicable tolerable limits for production and use limits for missile oxygen. Inasmuch as it was recognized that the problems of sampling and analyzing for impurities in liquid oxygen are difficult and that the utilization of realistic specifications for liquid oxygen require the selection of both sampling methods and analytical techniques suitable to fulfill the requirements, a study of methods of detection and analysis was included in the agenda. It involved a review of sampling procedures and devices, laboratory and field analytical procedures, and equipment.

Phase II of the program involved a review of the hardware and production system design concepts and the recommendation of factors relating to these concepts which will reduce or minimize contamination and facilitate the inspection and cleaning and increase operational study.

Phase III requested recommendation of definitive specifications of procurement storage or load limits or end use limits for missile liquid oxygen, including such quality control procedures as are necessary.

In May 1960 this program was expanded to cover an investigation of the sources and mechanisms for ignition of contaminated missile liquid oxygen. This included such experimental programs as were deemed necessary to verify existing data in this field. Such variables as rates of charge buildup, system geometry and dynamics of the phenomenon of static electricity in liquid oxygen systems were to be covered. Other possible sources and mechanisms for ignition such as were considered of importance were to be added. By this time, the peculiarities of the solid carbon dioxide, liquid hydrogen system has been noted, the possible effects of the existence of solid carbon dioxide in the missile fuel oxidant had been considered and a request for determination of the factors relating to solid contaminants, particularly solid carbon dioxide, were requested. This involved determination of the factors relating to the agglomeration of small crystals or particles of insoluble contaminants such as carbon dioxide and the heavier hydrocarbons, determination of their effect on oxygen systems, and recommendation of limits for operating conditions. Recommendations for proper operational conditions to reduce or eliminate the solid contaminants were also to be provided. This involved a thorough investigation to determine the relative merits of the different types of filters for removing solid material from liquid oxygen. Specific filters were to be recommended and if commercially available equipment was not suitable, design criteria were to be developed.

As a normal outcome of the work done to this point, Phase VI of the expanded program requested development of uniform cleanliness standards for oxygen equipment. Specifically declared beyond the

scope of this contract was the development of cleaning agents, equipment, and techniques. However, development and recommendation of suitable means of inspection and surveillance of liquid oxygen systems to assure proper cleanliness was required as was a study of methods of removing contamination from liquid oxygen at the storage site and the recommendation of the use of such techniques to reduce the disposal of contaminated oxygen and reduce the need for stringent cleaning requirements of oxygen systems.

In the study of the design concepts under Phase II of the original program, it became obvious that the liquid propellant safety manual did not provide safe handling instructions for the high pressure gases used in the ground support systems, therefore Phase VII of this program involved the production of three chapters for the Liquid Propellant Safety Manual covering safe handling procedures for high pressure gaseous oxygen, nitrogen, and helium.

As this study program progressed further it became obvious that there would be considerable advantage in having available data developed by an on-site sampling program which might be conducted at Cape Canaveral or Vandenberg. Supplemental Agreement No. 2 to the contract was then evolved and during January, February, and March of 1961 a continuous sampling and analyzing program was carried out with the sampling done using the Air Products sampler at Cape Canaveral and using the newly developed Multi-Contaminant Analyzer at the Research and Development Center at Emmaus, Pennsylvania for the analytical phase.

A Summary Progress Report was issued in July 1960 covering the first year's work. This final report includes that information and also the work done since July 1960 on the first and second supplementary agreements attached to the contract. Recommendations for additional work which should be performed are also included.

## II. DISCUSSION

This study was not aimed specifically at the understanding of the reasons for operational malfunctions. Rather, by logical evaluation of the potential role of contaminants, it was the intent to develop rational criteria for determining realistic limits for these contaminants in liquid oxygen as produced at the air plant, as delivered to the propellant-loading-system storage, after storage for various periods of time, and for reuse.

### SIGNIFICANCE OF CONTAMINANTS

#### Types of Contaminants

Three types of contaminants were of concern in this program:

- (a) combustible contaminants, solid or dissolved, which may constitute a fire or explosion hazard to both general safety and equipment;
- (b) solid inert contaminants which may contribute to mechanical malfunctioning of the propellant loading system or the rocket engine;
- (c) dissolved inert contaminants which may affect the rocket thrust or, under certain circumstances, might interfere with engine ignition.

#### Combustible Contaminants

Combustible contaminants are considered to be compounds which will react with oxygen upon suitable ignition, producing sufficient heat of reaction to raise the temperature of the reaction products to the ignition temperature. Typical combustible contaminants are methane, acetylene, and butane. In a few cases, notably acetylene and ozone, the heat of decomposition of the compounds themselves is sufficient to raise the temperature of the decomposition products to this temperature. This phenomenon will be discussed briefly in a following sub-section on "Initiation".

The hazards of combustible contaminants are obvious and of great importance. Considerable injury and damage from fires and explosions have resulted from the reaction of combustible contaminants in liquid

oxygen systems. Although emphasis in the following discussions may be placed on particular combustibles such as methane or acetylene, the statements made will generally apply to all combustibles.

### Dissolved Combustibles

In order to support ignition in liquid oxygen, dissolved combustibles such as methane, must be present in concentrations sufficiently high that the heat of reaction raises not only the reaction products but also the excess liquid oxygen to the ignition temperature. Thus, a limiting concentration called the "lower explosive limit" or "lower flammability limit" (LFL) is associated with the presence of insufficient fuel. Any concentration of combustible at or above this limit is flammable and, therefore, extremely dangerous and must be avoided. It should be pointed out that the LFL is affected by the external factors such as pressure, temperature, and type of ignition.

The LFL of a mixture of combustibles is a function of both the concentration and the LFL of each combustible in the mixture (21). The contribution of each combustible to the flammability of a mixture of combustibles may be deducted from the following approximate equation:

$$\frac{C_1}{L_1} + \frac{C_2}{L_2} + \dots + \frac{C_n}{L_n} = \sum \frac{C_i}{L_i} \approx \frac{C_m}{L_m} \quad (1)$$

where

$C_i = C_1, C_2, \dots, C_n$  = concentration of individual combustibles

$L_i = L_1, L_2, \dots, L_n$  = LFL of individual combustibles

$C_m$  = total concentration of all combustibles

$L_m$  = LFL of mixture

If  $\frac{C_m}{L_m} \geq 1$ , the mixture is equal to or exceeds the LFL.

This equation illustrates the principle of "additive contamination" which is discussed below, "Degree of Contamination". (See also Appendix A.) Although it was established for gaseous mixtures, it also applies to liquid solutions, even at liquid oxygen temperature.

#### Solid Combustibles

If the solubility limit of a contaminant in liquid oxygen is below the lower flammability limit, the liquid phase will not support combustion. However, if the contaminant is present in quantities greater than the solubility limit, a flammable hazard does exist due to the resulting fuel-oxygen slurry. Even the smallest grain of combustible solid in liquid oxygen has the potential of continued burning upon suitable ignition, and the concept of flammability limit, based on average concentrations, does not strictly apply. Although one small particle might not be dangerous in itself, a collection of such particles in liquid oxygen could be serious, since ignition may propagate from particle to particle. The hazard of solid combustibles can be avoided by preventing either the formation or accumulation of solid particles.

Acetylene historically has been the most important solid combustible contaminant and should receive special attention among all of the combustibles for several reasons. First, it is quite insoluble in liquid oxygen; second, it may show up in the air plant feed stream at concentrations above the ultimate solubility limit; and third, it is readily triggered into ignition. Although other solid combustibles may appear on occasion, i.e., residual solvents, the control of such materials depends on proper cleaning and inspection procedures.

#### Solid Inert Contaminants

Solid inert contaminants are considered to be small particles or fibrous materials, essentially insoluble in and unreactive with liquid oxygen. These contaminants are divided into two categories: insoluble material, such as rust and metal fragments derived from the equipment; and slightly soluble contaminants, particularly carbon dioxide and water, which are associated with the production and handling of liquid oxygen.

There are several hazardous characteristics of solid inert contaminants which should be considered.

First, and most important, solid inert contaminants may interfere with the mechanical operation of the system. Mechanical interference by solid contaminants is one of the most common causes of malfunctions in a LOX-handling system. These contaminants may cause the plugging of filters, lines, injectors, etc.; they may cause binding of mechanical movements by intruding into regions of small clearance; they may prevent valves from seating or flanges from sealing.

Second, the solid particles moving with the fluid stream may cause erosion within the fluid passages. Erosion produced by the abrasive action of the solid particles will usually be relatively minor, but in certain critical places where high velocities occur, such as at turbine blades, the solids can create considerable damage.

Third, the solid particles may accumulate static charges of electricity, which may discharge within the fluid. The accumulation of static charge will not cause damage by itself, but it is conceivable that a spark discharge originating from the static charge could initiate the reaction of combustible materials.

#### Dissolved Inert Contaminants

Dissolved inert contaminants are considered to be materials, such as nitrogen or argon, which are unreactive and quite soluble in liquid oxygen.

Nitrogen and argon are the principal dissolved inert contaminants in liquid oxygen. These contaminants are significant only to the degree that they serve as diluents for the liquid oxygen. Since missiles using liquid oxygen as the oxidant generally operate on the fuel-rich side, dilution of the oxygen will accordingly reduce thrust and the ultimate range or payload. A discussion of the effect on rocket range by the dilution of liquid oxygen with nitrogen can be found in a recent report (30). Argon will have a slightly greater effect than nitrogen on the specific impulse because of argon's higher molecular weight.

### Initiation

At the low temperature of liquid oxygen, chemical reaction rates are extremely slow. Even though a potential heat of reaction may be very high, spontaneous reaction rates are generally so slow that normal heat transfer mechanisms are sufficient to remove the small quantities of heat produced. However, the sudden addition of external energy to a local region can raise the local temperature and the reaction rate, resulting in a chain reaction when the heat released is greater than the heat absorbed by the surroundings. Such a reaction could easily become explosive. Initiation of a runaway reaction can be accomplished in a variety of ways, the more common including:

- a. Mechanical energy introduced in the form of friction or impact.
- b. Electrical energy introduced by spark discharge or resistance heating.
- c. External heat introduced by convection, conduction or radiation.
- d. Catalysts.

In some cases, the initiating methods cannot supply sufficient energy to complete the ignition process. However, if additional chemical energy is available from an easily-triggered source, such energy can act as a booster charge, causing the ignition to continue. Acetylene, ozone, and several other materials which may contaminate liquid oxygen have sufficient stored energy to act in this fashion. Further discussion of this point is presented in Appendix A.

### SOURCES OF CONTAMINATION

For purposes of illustration, Figure 1 is a simplified flow diagram of a typical liquid oxygen supply system from the air separation plant to the missile tank. A liquid oxygen supply system offers several opportunities for contamination. The major sources of contamination consist of: produced liquid oxygen; transfer operations; nitrogen pressurization. The minor sources of contamination will include: vent lines and relief valves; residual contamination; equipment deterioration.

————— PERMANENT (OR SEMI-PERMANENT) LINES  
 - - - - - CONNECT & DISCONNECT REQUIRED  
 ..... GAS LINE — PRESSURIZING OR VENT

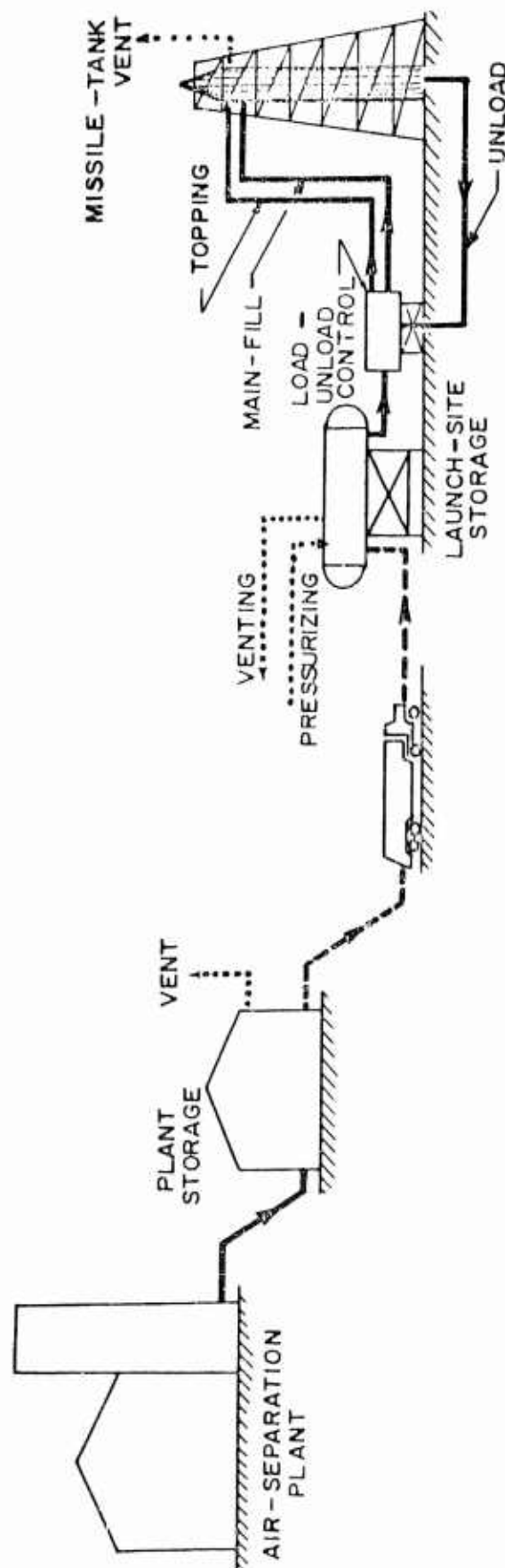


FIGURE 1. - SIMPLIFIED DIAGRAM: LIQUID OXYGEN SUPPLY SYSTEM

### Produced Liquid Oxygen

Liquid oxygen, as produced by the air separation plant and received by the plant storage tank, contains contaminants which have not been completely removed by the process used for separating oxygen from air. The ultimate source of most of this contamination is, of course, the air feed to the separation plant, and the quantity and variety of contaminants found in the liquid oxygen depend to a large extent on the effectiveness of their removal during the separation process.

Of the contaminants passed by the separation plant, the produced liquid oxygen contains a portion of the acetylene, the light hydrocarbons (less than C<sub>4</sub>), and other combustibles. A portion is removed in the waste nitrogen, and the remainder accumulates in driers, heat exchangers, and adsorbers. However, the liquid oxygen as produced must be considered as a major source for combustible contaminants. In addition, liquid oxygen as produced may contain carbon dioxide in varying amounts, and very small quantities of particulate matter from the hydrocarbon adsorbers.

### Transfer Operations

Whenever operations require the connection or disconnection of a transfer line, the opportunity for introducing additional contamination arises. At the time of connection, atmospheric contamination or dirt may be trapped in a section of the transfer line, to be carried into the system by the liquid. At the time of disconnection atmospheric contamination may deposit inside the cold transfer equipment, ready to enter the rest of the system during the next transfer operation. Field and laboratory experiments have shown that strong convective currents are formed by the density difference between cold oxygen vapors and warm ambient air. As the cold, denser vapors flow out of the low points of cold transfer equipment, the warm, less dense air flows in at the high points, depositing moisture and other condensables in the form of frost. This phenomenon occurs in a matter of seconds in the case of a transfer line with cold vapors flowing from the open end. It is suspected that much of the CO<sub>2</sub> contamination appearing in the oxygen liquid at its final point of analysis has entered via transfer operations.

### Nitrogen Pressurization

A third major source of contamination is the use of the nitrogen pressurization technique to transfer liquid oxygen from one tank to another. If it is assumed that only pure gaseous nitrogen is used for pressurizing, then the only contaminant introduced at this point is nitrogen.

### Vent Line and Relief Valves

Previously, it had been assumed that atmospheric contamination entered liquid oxygen systems through open vent lines and relief valves by a back-diffusion process. However, an experimental and mathematical study conducted under the present contract has indicated that contamination by back-diffusion is minor. This does not mean that atmospheric contamination cannot enter through vent lines; but only that there is no long-term persistent contamination. The amount of contamination introduced through vent lines by barometric pressure surges has not been established.

### Residual Contamination

Residual contamination in a liquid oxygen handling system may consist of cutting oils, solvents, and metal chips and other particles left from fabrication or cleaning operations. With strict adherence to proper procedures, there should be very little residue. However, mistakes and carelessness have resulted in unpredictable contamination.

### Equipment Deterioration

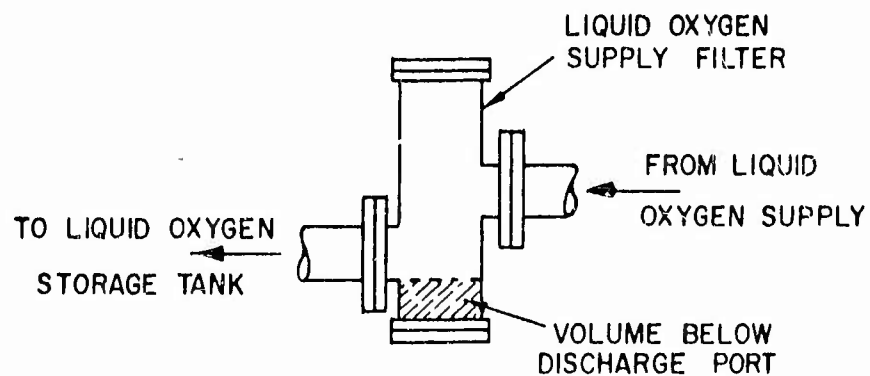
As with any complex mechanical equipment, long-term deterioration must be expected. Moving parts, such as valves and pumps, will wear and contribute to particulate contamination. In liquid oxygen systems, sources of such contamination will include: particles from filters, attrition of solid adsorbents, and erosion of metal parts by solids carried in the liquid oxygen stream. Although the quantities are small, these contaminants cannot be ignored.

## DEGREE OF CONTAMINATION

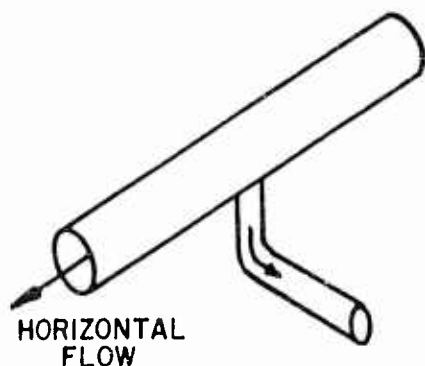
### Change in Contaminant Concentration

Missile liquid oxygen is handled at a temperature ( $-297^{\circ}\text{F}$ ) close to its boiling point, and the slight addition of heat will cause the oxygen to boil. The extremely low temperature of liquid oxygen means that heat will be supplied to it from the surrounding atmosphere and that it will be evaporating constantly. Dissolved contaminants with vapor pressures higher than oxygen, such as nitrogen, argon, and carbon monoxide, will vaporize more quickly than the oxygen, while contaminants with vapor pressures lower than oxygen, such as methane and acetylene, will vaporize less quickly than oxygen. Consequently, in a given amount of liquid oxygen, contaminants with high vapor pressure will decrease and contaminants with low vapor pressure will increase in concentration with the passage of time or with additional handling operations.

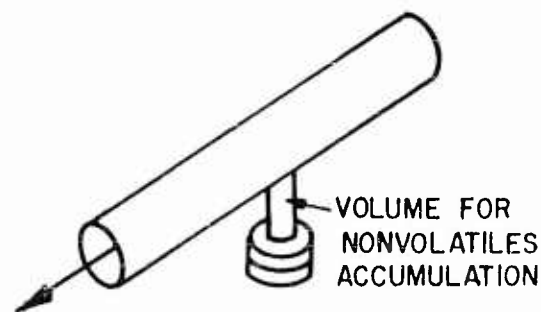
In many cases, the design of equipment and the arrangement of piping can magnify the problems of contamination either by encouraging local accumulation of solids or by creating isolated regions where local concentrations of contaminants can increase without disturbance by the main liquid oxygen stream. Usually, these conditions can be traced to inadequate mixing or to "dead-ending". Several examples of situations leading to solids accumulation are shown in the accompanying illustrations, Figures 2, 3, and 4. Figure 2 illustrates the type of small pockets which can act as traps for suspended solids. Figure 3 shows how a large quiet region can encourage the accumulation of solids. It is interesting to note that accumulations of carbon dioxide have been found in 28,000 gallon storage tanks which are in the proportions indicated in Figure 3. An example of the type of equipment arrangement which encourages the build-up of contamination is the liquid oxygen catch tank shown in Figure 4. In this case, liquid oxygen flows into the tank, but only vapor leaves the tank. This automatically leads to accumulation of less volatile contaminants.



(a.) LIQUID OXYGEN SUPPLY FILTER INSTALLATION



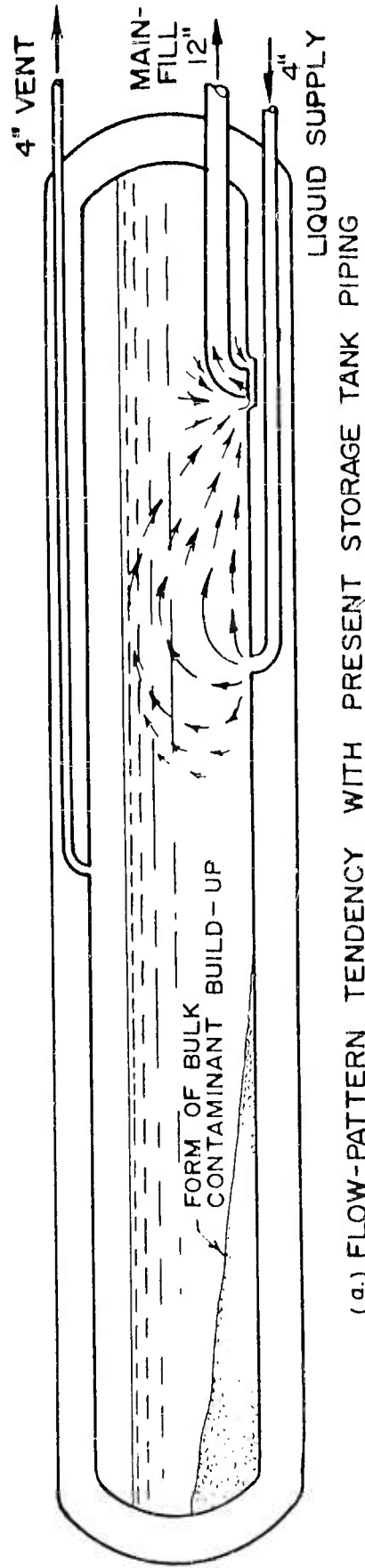
(1.) BEFORE MODIFICATION



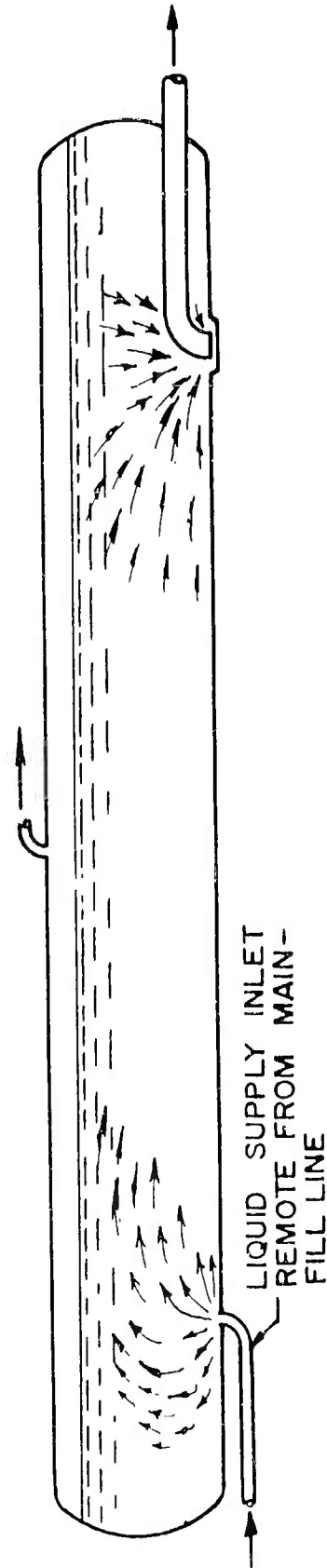
(2.) AFTER

(b.) AN EFFECT OF IN SITU PIPE MODIFICATIONS

FIGURE 2 - EXAMPLES OF PIPING DETAILS RESULTING IN  
CONTAMINANT CONCENTRATION BUILD-UP



(a.) FLOW-PATTERN TENDENCY WITH PRESENT STORAGE TANK PIPING



(b.) AN IMPROVED ARRANGEMENT

FIGURE 3 - FLOW LINES IN LIQUID OXYGEN LAUNCH-SITE STORAGE TANK

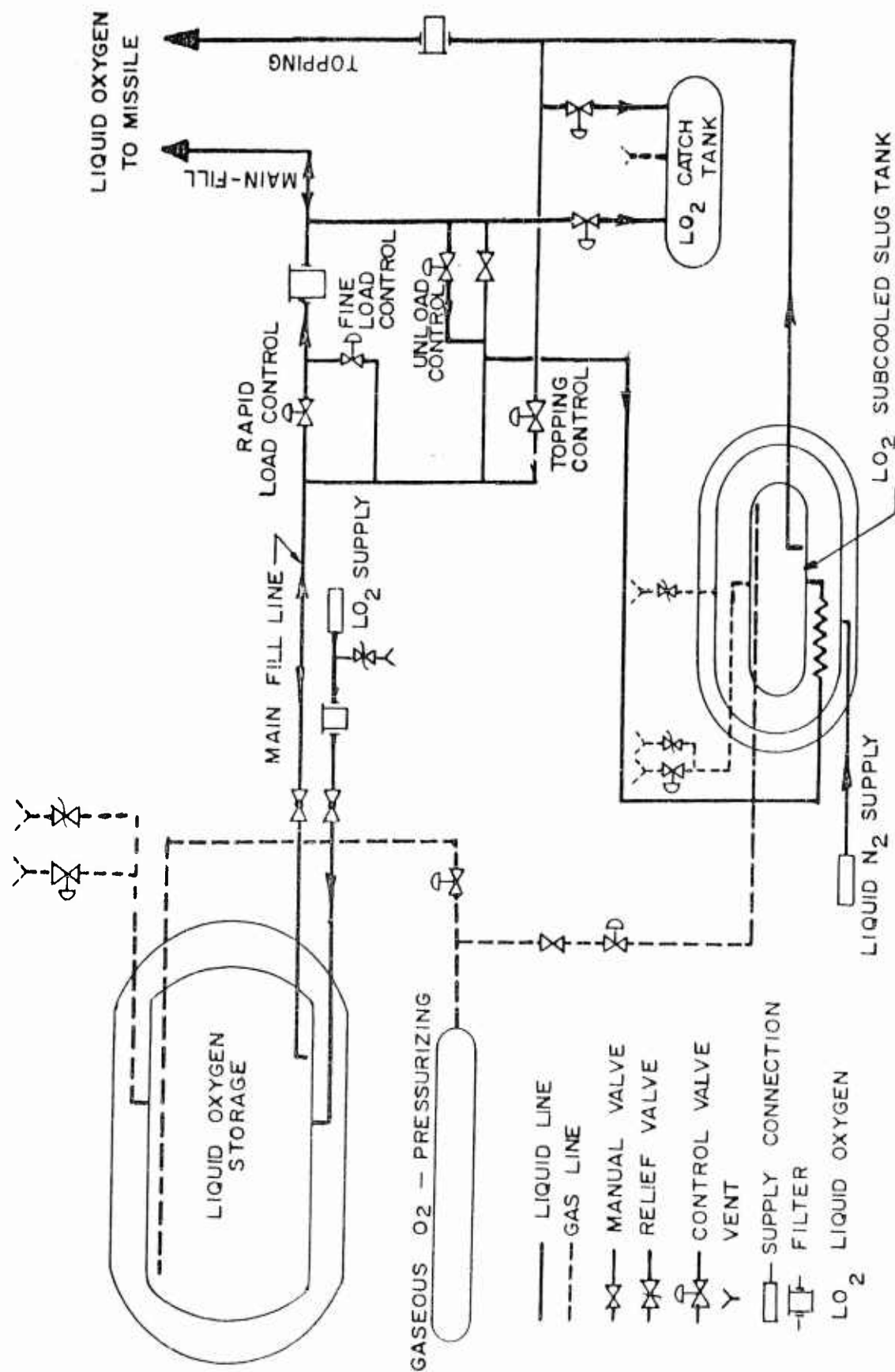


FIGURE 4 - TYPICAL LAUNCH-SITE LIQUID OXYGEN STORAGE AND LOADING SYSTEM

### Combustible Contaminants

All of the common combustible contaminants, except carbon monoxide, are less volatile than oxygen and consequently will increase in concentration as the liquid oxygen is vaporized. Thus, a safe concentration of a dissolved contaminant at the beginning can reach dangerous proportions by the time the oxygen is to be used. This means that the problem of controlling combustible contaminants would become more severe as the liquid oxygen passes through the supply system.

Of the potential combustible contaminants, the ones that are currently considered on a routine basis for analysis and control are the hydrocarbons and acetylene. Although other combustibles may appear as a result of unusual circumstances, the quantities are usually too small for routine detection. An analysis of the degree of contamination by combustible materials may be based on the following simplifications:

- a. The only combustibles of significance other than acetylene are the hydrocarbons.
- b. Acetylene is considered in a class by itself and not included in the hydrocarbons.
- c. Hydrocarbon molecules with more than four carbon atoms are reduced in the air separation plant to insignificant concentrations.
- d. The flammability limit is based on the total concentration of carbon atoms regardless of the type of hydrocarbon.

The principle of additive contamination, mentioned previously under "Significance of Contaminants", makes it possible to relate the combustible contaminants. The various combustible contaminants can be rated on the basis of their heats of combustion, with methane used as a reference standard. In the case of the hydrocarbons, which are assumed to be the only contaminants, the heat of combustion on a mole basis is roughly dependent on the number of carbon atoms in the compound. Since the flammability limit is a function of the overall heat of combustion, this limit will depend on the type of hydrocarbon supplying the carbon atoms. Consequently, all hydrocarbons can be conveniently calculated as methane equivalents and added together. Table I presents a list of analyses of liquid oxygen obtained from a number of representative plants, showing total hydrocarbons and acetylene. Total hydrocarbons are reported as methane equivalents in ppm by mole. It can be seen from Table I that, although total hydrocarbons are generally less than 50 ppm and acetylene is generally less than 0.25 ppm, in some cases concentrations may run somewhat higher depending upon local conditions. Table II presents in more detail some of the analyses shown in Table I. As can be seen, methane is the major combustible contaminant.

Although emphasis has been placed in this discussion on the flammability limits of combustible contaminants, it is important to note that specification limits are based on solubilities and not on flammability limits. Since it is not practical to identify the specific combustible contaminants in solution, it is necessary for reasons of safety to assume that the solubility of the "combustible" hydrocarbons (excluding acetylene, hydrocarbons of more than four carbon atoms, and non-hydrocarbon combustibles) is equal to a solubility of the least soluble hydrocarbon (four carbons or less). The least soluble "combustible" hydrocarbon is isobutylene which has a solubility of 560 parts per million methane equivalent.

TABLE I

OXYGEN CONTAMINANTS ANALYSES IN REPRESENTATIVE PLANTS\*

<u>Plant</u>	<u>Hydrocarbons**</u>	<u>Acetylene ppm (mole basis)</u>	<u>Carbon Dioxide</u>
<u>Liquid Oxygen Plants</u>			
A	12 to 18	< 0.5	3 to 6
B	4 to 35	< 0.01	0.5 to 1
C	21 to 27	< 0.25	0.5 to 4
D	15 to 25	< 0.25	15 to 30
E	24 to 26	< 0.25	21 to 24
<u>Gaseous Oxygen Plants (Liquid from Reboiler</u>			
F***	1 to 12	< 0.01	--
G	21 to 35	< 0.25	1 to 2
H	10 to 30	< 0.05	--
I	20 to 131	--	1,000 to 2,000
J	353	< 0.003	2

\* Based on information from private communications.

\*\* As methane equivalent.

\*\*\* Gaseous oxygen product.

## Insoluble or Slightly Soluble Inert Contaminants

### Insoluble (particulate matter)

The quantity of particulate matter resulting from equipment deterioration or poor cleanliness standards cannot be predicted with accuracy. A number of examinations have been made by investigators at different times with the desire to clarify the picture of particulate contamination.

Table III presents a summary of particle counts made from liquid-oxygen samples taken at Patrick Air Force Base over a period from July, 1957 through January 1960. These samples provide an indication of the ranges of particle sizes and counts, although unfortunately no information is available as to the location of the sample taps.

One examination of a plant storage tank revealed particulate matter in the form of dust accumulated at the bottom of the tank. Subsequent analysis of this material showed that it consisted principally of oxides of aluminum, iron, and silicon with a small amount of oil. Additional limited inspection showed little particulate matter in the storage vessels and piping beyond the plant storage tank. From the analyses, it appears that the dust resulted mainly from the hydrocarbon adsorbers. Although it is presumed that filters remove particulate matter down to particles less than 40  $\mu$  in diameter, at least one investigation (24) has found particulate matter larger than 200  $\mu$  in produced liquid oxygen. Particulate contamination should be small in the rest of the supply system if proper materials of construction are used and proper handling and cleaning procedures are followed.

### Slightly Soluble Inert Contaminants

In this category, only carbon dioxide will be considered, since it is almost always present and because measures taken to reduce CO<sub>2</sub> will be generally successful in eliminating the negligible quantities of other slightly soluble compounds.

TABLE II

CONCENTRATION OF DIFFERENT HYDROCARBONS  
IN REPRESENTATIVE OXYGEN PLANTS

<u>Plant &amp; Type</u>	<u>Hydrocarbons - ppm by mole as Methane Equivalent</u>			
	<u>Total*</u>	<u>Methane</u>	<u>C<sub>4</sub> or less**</u>	<u>C<sub>5</sub> or more</u>
A - Liquid	12 to 18	10 to 15	--	--
H - Gaseous	10 to 30	10 to 30	0	0
I - Gaseous	20 to 131	19 to 115	0.4 to 15	0.06 to 4
J - Gaseous	353	110	243	Traces

\* Excluding acetylene

\*\* Excluding methane

TABLE III

PARTICULATE MATTER IN LIQUID OXYGEN\*

<u>Sample Source</u>	<u>Minimum and Maximum Particle Count for Micron Sizes**</u>			
	<u>10-20</u>	<u>20-40</u>	<u>40-80</u>	<u>80</u>
ABMA	480 - 6540	120 - 1860	120 - 1080	14 - 120
Complex 14	780 - 1740	290 - 300	26 - 180	8 - 14
Convair	120 - 9780	53 - 1200	12 - 900	0 - 240
Douglas	720 - 17400	85 - 5640	0 - 1680	0 - 240
Martin	4020 - 15360	600 - 1140	240 - 540	24 - 36
PAA	220 - 9480	40 - 3060	0 - 780	0 - 100
Vanguard	660 - 11400	120 - 2580	60 - 480	6 - 72
Thor-Able	3360	1380	420	180
Patrick Plant	420	50	50	20

\* Samples analyzed at Patrick Air Force Base during the period July, 1957 through January, 1960.

\*\* Sample size - 100 ml of liquid oxygen.

The solubility of carbon dioxide in liquid oxygen (3, 9, 15) is presented in Figure 5. It can be seen that, at the usual storage and handling temperature ( $-297^{\circ}\text{F}$ ) of liquid oxygen, the solubility of  $\text{CO}_2$  is about 4.5 ppm. As explained previously, any concentration of  $\text{CO}_2$  above the solubility limit is undesirable, but analytical data show that such conditions do exist in liquid oxygen supply systems. Limited field data at launch and test sites (2, 23) show that stored liquid oxygen contains  $\text{CO}_2$  in the range of 12 to 300 ppm. Carbon dioxide is normally present in the air feed to oxygen plants at concentrations of about 300 ppm. Although most of the  $\text{CO}_2$  is removed in the separating process, the commercial use requirements and economics of liquid oxygen manufacture do not require the complete removal of  $\text{CO}_2$ . The figures shown in Table I should not be taken as representative of the range of possible  $\text{CO}_2$  contamination in produced liquid oxygen. The lower concentrations indicated may be routinely obtained through suitable plant operation. A further limitation on the figures of Table I is placed by the difficulty of obtaining a representative sample of suspended solids.

If liquid oxygen contains  $\text{CO}_2$  dissolved to the saturation point, slight changes in temperature or pressure may cause  $\text{CO}_2$  to precipitate. Precipitation can be induced by a sharp decrease in pressure, such as might occur at a valve or orifice, or solid  $\text{CO}_2$  might appear by flash evaporation of the liquid oxygen at a local hot-spot. A mathematical analysis of the time required to dissolve  $\text{CO}_2$  particles in liquid oxygen showed that, once solid  $\text{CO}_2$  has precipitated out of solution, it is difficult to redissolve the precipitate even though the liquid oxygen may no longer be saturated with  $\text{CO}_2$ . The large difference between the rate of precipitation and the rate of re-solution can easily result in the build-up of solid  $\text{CO}_2$  in quiescent regions.

Even if carbon dioxide is not present initially, every transfer operation exposing cold internal parts to the atmosphere will introduce  $\text{CO}_2$ . The quantity of  $\text{CO}_2$  introduced with each transfer operation depends on the operator and on the procedures followed. To further aggravate the problem, the continuous vaporization due to heat leak to stored liquid oxygen increases the concentration of  $\text{CO}_2$ .

CARBON DIOXIDE CONCENTRATION, MOLE PPM

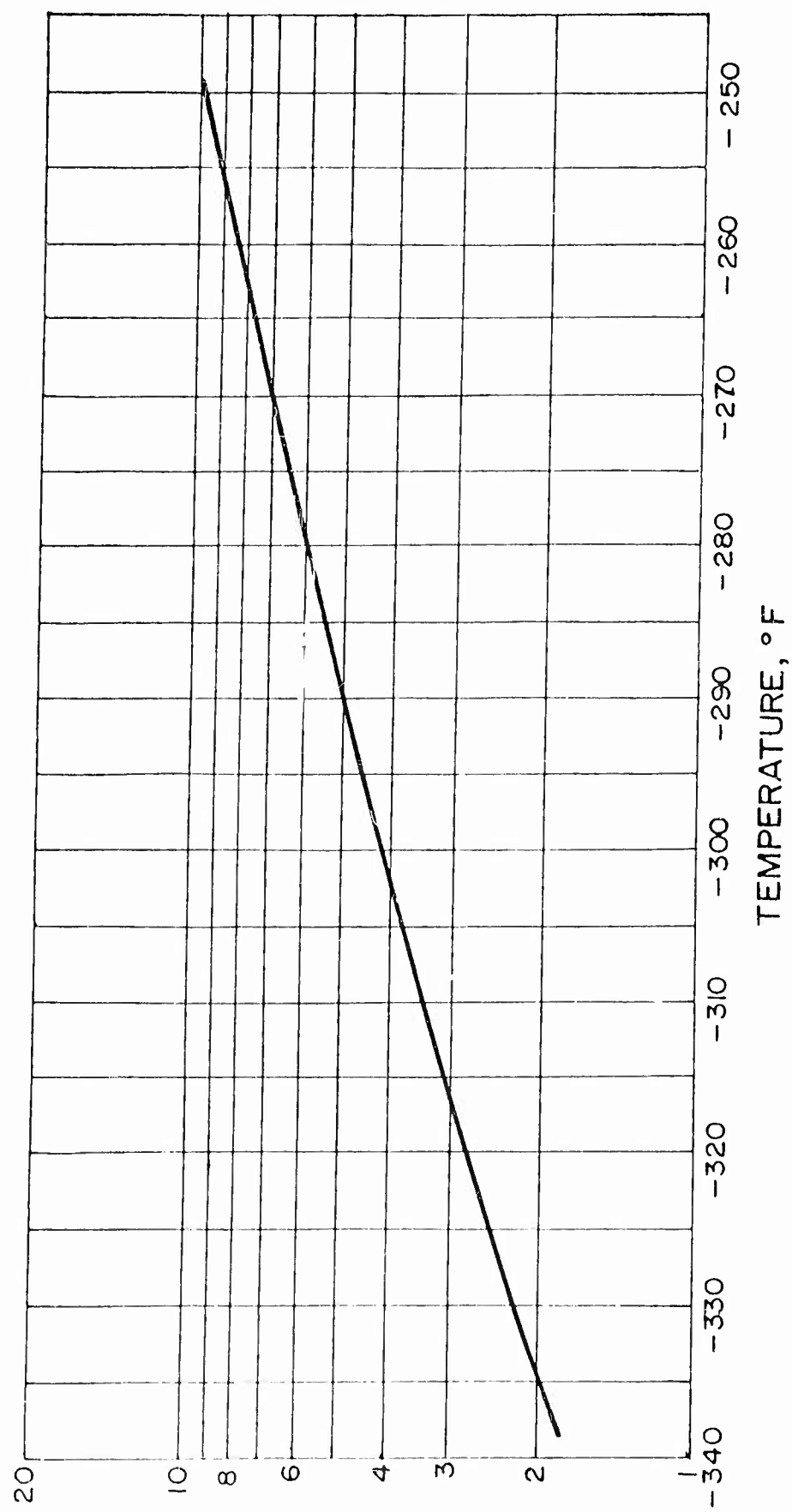


FIGURE 5 - SOLUBILITY OF CARBON DIOXIDE IN LIQUID OXYGEN (7, 8, 9)

### Miscible Inert Contaminants

Nitrogen and argon are the only miscible contaminants of importance. Since the only source of argon contamination is the liquid oxygen produced in the liquid oxygen plant, no increase in the argon contamination can occur after the oxygen enters plant storage tanks. The initial concentration of argon in the produced liquid oxygen is not permitted to rise above 5000 ppm (0.5%), this quantity comprising the bulk of the contamination existing in the liquid oxygen. Since argon is slightly more volatile than oxygen, the argon concentration will decrease slowly by preferential vaporization as the liquid oxygen passes through the supply system. This decrease in concentration is illustrated in Figure 6 where it can be seen that the degree of argon contamination changes only slightly throughout the lifetime of the oxygen liquid.

The amount of nitrogen in liquid oxygen as received from an oxygen plant is relatively low. As is the case with argon, the nitrogen content will also decrease by preferential vaporization, although much more quickly. The vaporization rates of the two contaminants can be compared in Figure 6 where it can be seen that the change in nitrogen concentration is much greater than the change in argon concentration.

The major source of nitrogen contamination during transfer and storage is the use of gaseous nitrogen pressurization to transfer liquid oxygen. There has been some disagreement on the amount of contamination from this source (29, 30), but the experimental evidence shows that the resulting contamination by nitrogen can be tolerated for most missions. In addition to the references quoted, experimental work performed under the present contract showed the slight degree of contamination by nitrogen due to pressurization.

### CURRENT SPECIFICATIONS FOR LIQUID OXYGEN AND EQUIPMENT

#### Liquid Oxygen Specifications

Liquid oxygen is procured for missile use according to Military Specification MIL-P-25508-C USAF, dated November 7, 1960. This specification

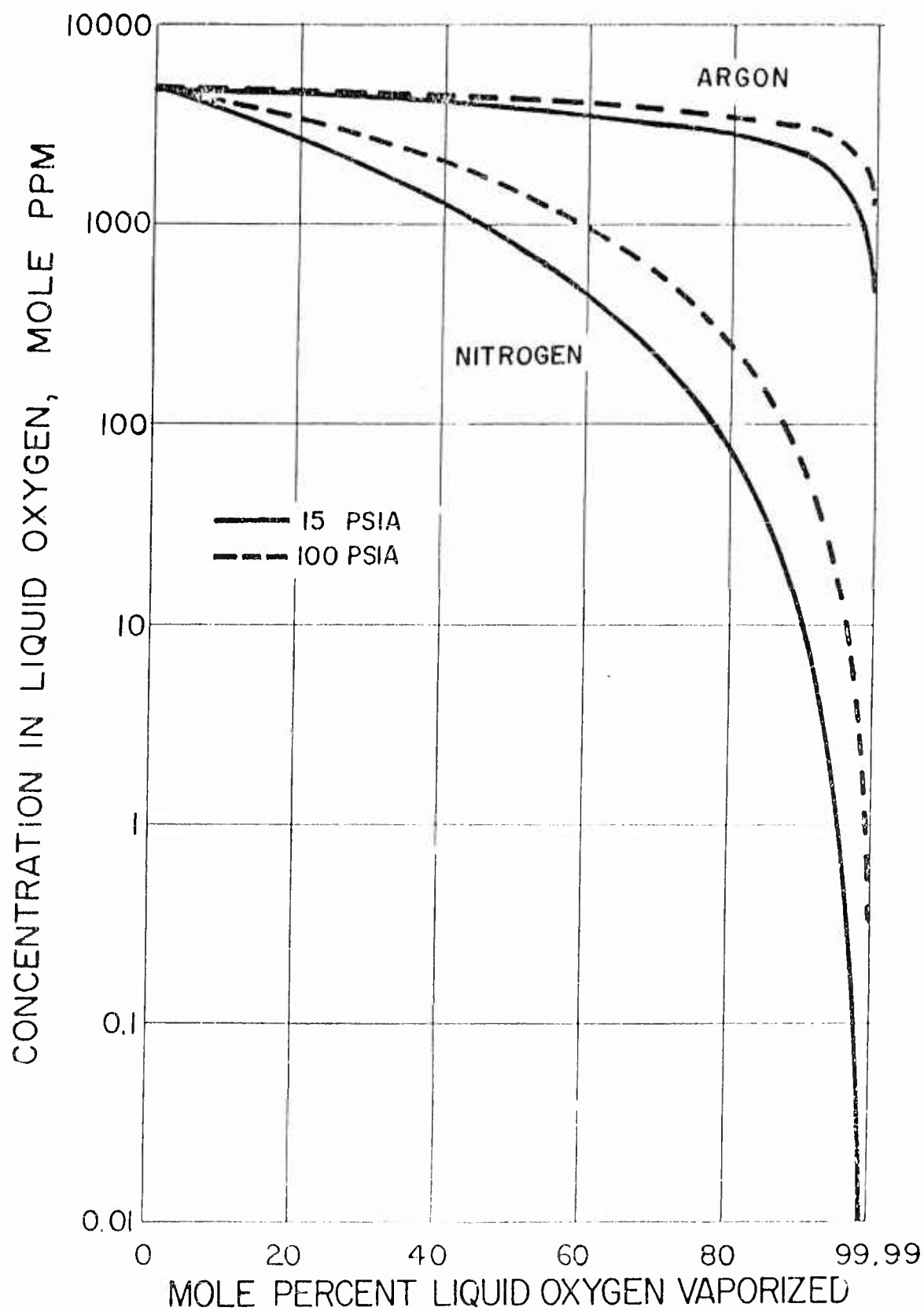


FIGURE 6 - DIFFERENTIAL VAPORIZATION OF 99.5% LIQUID OXYGEN:  
EFFECT ON CONCENTRATION OF MORE VOLATILE CONTAMINANTS

requires that the purity of the liquid oxygen, when gasified, shall contain not less than 99.5 percent oxygen by volume. The remaining 0.5 percent is mostly argon. The combustible and relatively insoluble impurities contained in liquid oxygen as produced and procured are limited to the parts per million range, as dictated by process and safety considerations in liquid oxygen manufacture.

These tentative procurement and use limits, presented in Table IV, were established as a result of a series of conferences including rocket engine manufacturers, military representatives, liquid oxygen producers, and advisors (1, 8, 11 through 14, 28, 31).

Initially the total hydrocarbon procurement limit was set at 75 ppm by weight as carbon, and the use limit at 225 ppm by weight as carbon, to permit a maximum of three-fold concentration of impurities. More recently the procurement total hydrocarbon specification was reduced to 25 ppm by weight because liquid oxygen producers can, and are supplying product of this quality. The use limit was not changed.

These limits define concentration as parts per million on a weight basis, but there has apparently been some confusion as a result of the use of this convention. A concentration of 225 ppm by weight, measured as carbon, is equivalent to 600 ppm by mole measured as carbon. Liquid oxygen manufacturers consider 500 ppm by mole to be the maximum safe limit and will stop operations before this value is reached. If the 225 ppm is on the mole basis, the value is entirely consistent with non-hazardous operation.

It is believed that the total hydrocarbon concentration should be defined in more explicit terms to avoid confusion. For example, n-pentane, a hydrocarbon, has a solubility in liquid oxygen of 200 ppm by mole, as carbon. At 225 ppm by mole, this hydrocarbon would represent a hazardous condition. The 500 ppm by mole maximum safe limit recognized by liquid oxygen producers applies only to hydrocarbons containing four carbon atoms or less, excluding acetylene compounds.

Therefore, it is assumed in this report that the interim limits meant ppm by mole measured as methane or carbon (on a mole basis the numerical value will be identical for either). Further, the total hydrocarbons will be interpreted as C4 or less hydrocarbons.

TABLE IVLIQUID OXYGEN INTERIM SPECIFICATIONS

MIL-0-25508A USAF (June 21, 1957)

	<u>Procurement</u>	<u>Use</u>
Oxygen, percent by volume - minimum	99.5	--
Total Hydrocarbons, ppm by weight - minimum	25 as Methane	225 as C
Acetylene, ppm by weight, maximum	0.5	1.5
Moisture, dewpoint °F - maximum	-65	--
Filterable Solids		
Filter Rating, microns	10	40
Filter Absolute, microns	40	72
Maximum Solids, mg/liter	2.5	2.5

## Equipment Cleanliness Specifications

### Propellant Loading System

Standards of cleanliness for propellant loading systems have been defined in specifications issued by Headquarters, Air Force Ballistic Systems Division. For liquid oxygen, these specifications, presented in Table V, require that the effluent liquid oxygen from the system shall not exceed the limits set for total hydrocarbons, acetylene, and solid particles.

The 25 ppm by weight total solid particles limit of these cleanliness specifications is equivalent to 2.9 milligrams per liter of oxygen as compared to 2.5 milligrams per liter specified by the interim procurement and use limits. (Fuel propellant loading systems are limited to ten times this amount of solid particles.) The equipment particle size is limited to a maximum dimension of 150 microns while the interim procurement and use limits specify 40 and 72 microns absolute, respectively. These differences could result in the propellant loading system contributing solid contaminants to liquid oxygen in excess of the use limit for the latter.

### Rocket Propulsion System

Manufacturers of rocket propulsion systems (1) specify the limits presented in Table VI for the liquid oxygen hardware components of the missile. These specifications are broader than those for the loading system. Conceivably, liquid oxygen loaded into the missile could on return to the launch-site support equipment contaminate the latter to a point that it is in excess of its cleanliness specifications.

## SUPPLEMENTAL AGREEMENT NO. 1

### Sources and Mechanisms for Ignition

Ignition of a nonhypergolic system requires a combustible system and a source of energy. Probable ignition initiators found in liquid oxygen systems are not highly energetic. Liquid oxygen systems can detonate by initiating a combustion wave with a weak ignition source. This com-

TABLE V

CLEANLINESS SPECIFICATIONS FOR LIQUID OXYGEN  
PROPELLANT LOADING SYSTEMS

Maximum Limits of Contaminants in Flushing Liquid Effluent

Total hydrocarbons, by weight as carbon	75 ppm
Acetylene (Illosvay method)	1.0 ppm
Total solid particles (by weight)	25 ppm
Particle distribution	None over 150 microns*
Water content	None

\*Liquid oxygen used for the system test must be prefiltered through a 10 micron filter.

TABLE VI

CLEANLINESS SPECIFICATION FOR LIQUID OXYGEN HARDWARE  
IN ROCKET PROPULSION SYSTEMS

Hydrocarbon per square foot	8 mg. maximum
Solid particles - total	10 mg. per liter maximum
- distribution:	

Particles

<u>Longest Dimension - microns</u>	<u>No. of Particles Allowed</u>
0 - 300	No limit by count
300 - 500	5 per 100 ml of liquid
500 - 1000	1 per 100 ml of liquid
over 1000	No particles allowed

Fibers

<u>Dimension - microns</u>		<u>No. of Fibers Allowed</u>
<u>Length</u>	<u>Maximum Diameter</u>	
0-750	25	No limit by count
750-2000	25	20 per 100 ml of liquid
2000-6000	40	2 per 100 ml of liquid
Over 6000	--	No fibers allowed

bustion wave can in turn initiate a detonation in the bulk of the liquid oxygen system.

#### General

The range of energies needed for ignition in liquid oxygen system and the range of energies available from possible ignition mechanisms are wide. It is unlikely, however, that in most cases the ignition energies will be greater for the bulk of the system than what is available from the ignition mechanism. In these cases ignitions of the bulk system can be caused by a secondary mechanism; a weak igniter, igniting a local sensitive mixture, which in turn can initiate a detonation wave in the bulk of the liquid oxygen system. Particular efforts should be made to eliminate sensitive, low ignition energy, contaminants, such as acetylene or fuel films.

Electrostatic charge accumulation and discharge are common hazards in handling flowing liquids, especially liquid fuels. Normal safety practice dictates that all portions of the storage and transfer systems must be electrically grounded. Sloshing of the liquids must be held to a minimum as the moving of the liquid, a poor conductor over the tank surfaces, also a poor conductor, causes ions and electrons to cross from one surface to the other. This results in generation of equal and opposite charges on the surfaces.

Pure liquid oxygen is, in itself, a very poor conductor. However, small amounts of polar impurities increase the conductivity considerably. The hazardous range of conductivity is from  $10^{-11}$  to  $10^{-15}$  mhs/cm. Geometry of the system, flow characteristics, (i. e. 2 phase vs. 1 phase) elect. properties of the components of the system and the nature and amounts of the impurities all contribute to the hazard. Please refer to Appendix D for a detailed explanation of the static phenomenon.

### Sources of Ignition

Carbon steel pipe or container can burn in pure oxygen, as the flame temperature is higher than that of the melting temperature on the oxide formed by the reaction. Initiation, however, requires attainment of steel melting temperature by the initiator.

Homogeneous solutions in liquid oxygen can exceed flammability limits (19).

Poorly miscible contaminants, such as acetylene, can exist as a solid dispersion in liquid oxygen.

Lubricants from compressors and valves, and fuels seeping through common pressurizing systems, can build up a surface coating on pipes and containers.

Ozone has not been detected in liquid oxygen in dangerous quantities. The possibility exists, however, that ozone can be generated and concentrated in one spot in a liquid oxygen system.

Non-combustible solids may enhance the ignition hazard in a combustible system by functioning as hot spots, reaction catalysts, or a surface for electric charge separation in a flowing system.

### Ignition Mechanisms

#### Sparks

Sparks can evolve from unshielded electrical equipment or by electrostatic discharge.

#### Impact

Impact can be induced by a shock wave due to sudden opening or closure of valves and relief devices, or by friction of sliding surfaces in a valve, pump bearings, or slip flow of solids in the liquid stream. Impacts usually cause ignition through secondary mechanisms; by adiabatic compression of minute bubbles or by heating of grit particles or surface defects.

### Catalysts

Solid or solidified impurities can catalyze exothermic reactions that will develop into flames or detonations.

### Energy Considerations

The minimum ignition energy of volatile solvents in gaseous oxygen is of the order of 0.2 millijoules (18). Activated carbon soaked in liquid oxygen required 2 to 30 Joules for spark ignition (27) and 20 to 500 Joules for ignition by impact. The maximum range of ignition energies for LOX systems is, therefore,  $10^{-4}$  -  $10^{+3}$  Joules.

It has been shown (19) that the lowest flammability limit of methane and ethane are higher in LOX than in gaseous oxygen. The large heat sink available in LOX requires more energy from the combustion reaction to maintain combustion. By the same token more energy will be required for ignition in homogeneous mixtures of a combustible with LOX than with gaseous oxygen.

In a heterogeneous system, such as a film or pool of combustible on the surface of a pipe, a solid, or a container, the increase in rate of diffusion of oxygen to the reaction zone (due to the large concentrations of oxygen at close proximity) may offset the cooling effect of the LOX, and ignition energies may be of the same order of magnitude as with gaseous oxygen.

In our work on ignition of hydrocarbon films in gaseous and liquid oxygen, observations showed that a ring was burnt around the pipe surface, centered at the location of the igniter. The film ignited and the flame propagated a short distance before being quenched by the cooling effects of the cold surface and the liquid oxygen.

The rate of energy application is another important consideration. As the rate of energy application decreases, the ignition energy increases (26). This effect is mostly a function of the geometry of the igniter and is governed by the rate of heat losses from the ignition zone.

### Spark

An electrostatically generated spark will give up  $10^{-6}$  to  $10^{-7}$  Joules, depending on the electrical conductivity of the system. Discharge time is fast, about  $10^{-7}$  sec (17) and calorimetric experiments established that 85% of spark energy is available for ignition in the form of heat (17).

### Impact

Ignition by impact alone requires a large amount of gross impact energy (6) unless a secondary mechanism can operate.

Sliding impacts can generate a temperature elevation of  $1000^{\circ}\text{C}$ , for  $10^{-4}$  sec, in a piece of grit on the surface, or in a defect in the surface (7). The presence of a liquid film on the surface requires greater impact energies to generate hot spots, but does not prevent their generation. Poor thermal conductors require less energy to form a hot spot, than good conductors and the maximum temperatures attainable are limited by the melting points of the surfaces. A hot spot one millimeter in diameter, 0.5 mm thick in a steel surface can give up 20 m.j. when it is cooled by  $10^{\circ}\text{C}$ . The amount of energy available from a hot spot is limited by heat transfer considerations, unless the hot spot is generated in a combustible particle.

An adiabatically compressed bubble of oxygen, one mm in diameter, compressed from 20 psia to 2600 psia, starting at  $100^{\circ}\text{K}$  will acquire approximately 1 m.j. of energy.

### Catalysis

A catalyst can reduce the ignition energy by decreasing the activation energy of the overall reaction. It can also serve as a heat sink and prevent the formation of a hot spot. This depends on the material, geometry and size of particle. Smaller particles are more hazardous as catalysts than larger particles.

## Hydrocarbon Film Ignition Tests

### General

Ignition of hydrocarbon film which exist on the wall of piping or vessels in gaseous oxygen service is of major interest to all who are involved in the handling of oxygen.

The tests conducted under this program were particularly designed to aid in the determination of a reasonable safety limit for the concentration of hydrocarbons on the surface of ground support equipment or piping to be used in lieu of the 4000 microgram per square foot (mcg/sq ft) standard developed by LeSuer and Williams (16) in their interim standard report. This level of contamination was based on tests run at Cape Canaveral Missile Test Center using RP-1 as the contaminant. RP-1 is highly combustible and consequently promoted a safe upper limit which may be excessive when a normal lubricant is considered. A 4000 mcg/sq ft concentration is a ostensibly clean dry surface.

Palmer (20) reported work performed by Loison in 1952. These tests were performed with an oil concentration of about 20,000 milligrams per square foot and a long (200 to 300 ft) pipe under 100 psig air pressure. This combination ruptured the pipe. Therefore, the area of present interest is between 4 mg/sq ft and 20,000 mg/sq ft.

Basyrov and Mikhedov (4) studied the detonation limits of some Russian lubricating oils solidified and dispersed in liquid oxygen at concentrations of 7.5 to 21% oil in LOX. For one type of spindle oil in a mixture of 15% oil in LOX, the detonation ability was similar to that of TNT.

Some unsystematic work had been done at Air Products and Chemicals, Inc. in 1956 and 1957 (3), on ignition of a variety of lubricants in air, oxygen, and liquid oxygen. The amounts of oil were substantial and powerful detonators were used. The sound of the detonation and a study of the surviving parts of the equipment indicated that the oil ignited in all tests. No quantitative data of the oil film concentrations were taken.

### Equipment Description

Figures 7 and 8 shows the test vessel used for these experiments. It was a 2-foot section of 1-inch stainless steel pipe with two 6-inch long 1/2-inch diameter sections at each end which had provisions for the introduction of a solution of hydrocarbon (n-hexadecane) in carbon tetrachloride. The ignition was provided by either a spark coil connected to the electrode or by an electric match inserted at the center of the pipe. N-hexadecane was chosen because it is a common component of lubricating oils and because a single hydrocarbon is more easily analyzed than a mixture. Figure 9 is a photograph of a typical test assembly.

### TEST PROCEDURE

A n-hexadecane film was applied evenly to the surface of a clean section of pipe. The boiling temperature and the molecular weight of n-hexadecane are in the ranges for common lubricants; it is available at a purity of at least 95% and its concentration in solution can be determined with accuracy.

The pipe section (Figures 7 and 9) was 2 ft of 1 inch schedule 40 stainless steel pipe with a 6-inch section of nominal 1/2 inch stainless pipe at each end. During gaseous oxygen runs, one end of the pipe was closed by a rupture disc made of 1.5 mill. brass foil in a modified 1/2 inch union. These discs were rated at 400 psig. A rupture disc that was rated at 2000 psig was used for the 1500 psig runs.

The hexadecane was applied to the surface from a solution in carbon tetrachloride, which was evaporated in a hot water bath while rotating the pipe section to achieve uniformity of the hydrocarbon film on the surface. Visual and tactile observation indicated that a reasonable degree of uniformity was achieved. The amount of hydrocarbon deposited on the surface was controlled by the quantity and concentration of the feed solution. The area covered was calculated to be 0.723 sq ft.

Two ignition mechanisms were used:

The first mechanism was a high voltage spark. A Model-T Ford ignition coil was used with an electrode made either from a length of nichrome wire in a compressed Teflon insulator, or a copper wire soldered to the tip of a spark plug. The electrodes were in-

serted at the middle of the pipe and the tip of the wire was maintained at a distance of 5 mm from the opposite pipe wall, which served as the grounding electrode. The power input to the spark coil was 5 to 12 watts.

The second mechanism used was an electric match, DuPont S-65 squib. The squib was stripped of its insulation, re-insulated with ceramic beads, and positioned at the end of the 1" pipe section. This squib releases 4 to 8 calories in about 20 milliseconds.

After application of the film, the pipe section was cooled to room temperature and the igniter and the oxygen line were connected. The pipe was then purged with oxygen for five minutes to remove the last traces of the solvent vapors. The rupture disc assembly was then tightened, the pipe was pressurized with oxygen, and ignition was instigated. The same procedure was followed for the blank runs except that ignition was not started and the pipe was pressurized at 50 psig for five minutes.

The pipe section was then disassembled. The unburned hexadecane was dissolved in two 125 cc batches of fresh carbon tetrachloride and the combined solution was concentrated by evaporation of most of the solvent. The volume of the concentrate was measured and the concentration of the n-hexadecane was determined with a Beckman IR-4 infrared analyzer.

For the runs in liquid oxygen, the end sections were removed after deposition of the film and one end of the 1-inch section was capped (Figure 8). The area of the section was calculated to be 0.548 sq ft. The pipe was immersed vertically in liquid nitrogen contained in a stainless steel dewar. Gaseous oxygen was fed into the top of the pipe and liquid oxygen was condensed to fill about 80% of the volume. By using this condensation technique in contrast with previous experiments in which liquid oxygen had been poured into warm containers, only a small amount of oxygen was present in case a detonation would be initiated. Thick electrical insulation was used on the high voltage line and the pipe itself to prevent current leakage. Following ignition the pipe was removed and warmed slowly. The residual hexadecane was dissolved in carbon-tetrachloride, concentrated, and analyzed.

The pipe section was disconnected and opened. The remaining film was dissolved in two 125 cc batches of fresh carbon tetrachloride. This

solution was concentrated by evaporation of most of the solvent in a standard Pyrex evaporation unit, and the n-hexadecane in the concentrate was determined.

### Discussion of Results

The results, plotted as surface concentration of hexadecane (mg/sq ft of pipe surface) against the percent recovery of the hexadecane, are given in Figures 10 through 12.

Since all ignition work is generally poorly reproducible, a number of runs were made at each concentration and the results were plotted in a statistical form instead of showing the individual points. The plot for each concentration represents the 95% confidence limit of the results and was calculated by the relation  $\bar{X} \pm \frac{s}{n^{1/2}}$ , where  $\bar{X}$  is the average per cent

of unburnt hexadecane recovered in all the runs at that concentration,  $s/n^{1/2}$  is the standard deviation for these runs and  $n$  is the number of runs. The number of runs is also given on the plot. These data and the results of the individual runs are also given in Table VII.

In Figure 10 the 95% confidence limit of all 11 blank runs is  $99.3 \pm 5.7$ . The spread of the squib ignition runs is greater, since a small area that burns under the igniter is not reproducible.

The infrared analyses of the hexadecane in the carbon tetrachloride were reproducible to 0.3 mg/cc. This uncertainty could cause a deviation of 2% in the recovery in the 1000 mg/sq ft range and a deviation of 15% in the 100 mg/sq ft range. This is the probable reason for the larger scatter of the data at lower concentrations.

At the highest surface concentrations used, there was not sufficient oxygen at 50 psig to burn all the hexadecane. The two broken lines on Figure 10 indicate the minimum recovery of hexadecane for the two concentrations, if all the oxygen at 50 psig is consumed in a stoichiometric ratio to form only  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as combustion products. Actually, some carbon is formed in all ignition runs and considerable amounts of carbon were found in the high concentration runs. In the two highest concentration runs at 6000 mg/sq ft a detonation wave followed the ignition. Subsequent runs were made at lower concentrations.

### Effect of Pressure

No significant effect was found in the range of 20 to 200 psig. In ten runs made at 1050 mg/sq ft and 1500 psig, the recovery was  $83 \pm 6\%$ , compared to a recovery of  $99 \pm 3\%$  for ten runs at the same concentration and pressures of 20 to 200 psig. Increased pressure is known (5) to decrease the ignition temperature of lubricating oils and the increased solubility of oxygen in the oil film probably helps to propagate combustion.

### Effect of Ignition Mechanism

Combustion properties of the system hexadecane-oxygen were estimated from the literature (10, 22, 25). The quenching distance was estimated to be less than 4 mm. Therefore, the sparking electrode was kept at a distance of 5 mm from the wall. The minimum ignition energy was estimated to be  $6 \times 10^{-3}$  cal. The ignition energy of both ignition mechanisms used was considerably higher. The energy of the spark was of the same magnitude as friction or impact effects that are possible sources of ignition in a pipe system. The rate of application of the ignition energy of the electric match is several orders of magnitude greater than that of the spark. There is, however, no way of directly comparing different ignition mechanisms. It is very unlikely though that self-ignition in a LOX system will be instigated by a source as powerful as an electric match.

The data in Figure 11 on the results of ignition by an electric match show no marked significances from the data in Figure 10, except for poorer reproducibility. Possibly more hexadecane directly under the squib was burned.

### Effect of Temperature

In about one-fourth of the runs using spark ignition, the tube was deliberately not allowed to cool after evaporation of the solvent. The temperature of the pipe was 30 to 40 degrees Centigrade above ambient temperature. No effect of temperature in this range was found

At liquid nitrogen temperatures, the hydrocarbon film on the surface of the pipe freezes, and a small amount of film flakes off. The frozen oil,

being less dense than the LOX, floats to the surface creating an increased hazard.

Blank runs were made to evaluate the magnitude of this effect. The freezing, flaking, and floating mechanism was not large below concentrations of 500 mg/sq ft (Figure 12).

In the liquid oxygen runs, the inside of the pipe was observed before and after ignition. At a hexadecane concentration of 1000 mg/sq ft, a bright ring about 2 inches long, symmetrical about the sparking electrode, was observed. This indicated that ignition had started but did not propagate. No such rings were observed in the blank runs. At lower concentrations, small patches of clean areas were observed under the electrodes after ignition but no continuous burned region was evident.

#### Effect of Lubricant Flow

At surface concentrations of over 1000 mg/sq ft, some mobility of oil on the surface was observed. It seemed likely that at high surface concentrations some of the film would flow to the lowest parts of the system, accumulate, and increase the ignition hazard at that location.

Some experiments were made to determine the concentration level at which this effect becomes pronounced. A tray was constructed from a 3/16-inch flat stainless steel plate (0.80 sq ft surface area). Thin walls were connected, using an epoxy resin adhesive. The surface was coated successively with 100, 250, 500, 1000, and 2500 mg/sq ft of n-hexadecane by applying predetermined amounts of 20 mg/cc solution of hexadecane in carbon tetrachloride. The solvent was evaporated using an infrared lamp. Smear tests were made at each concentration by rubbing a finger on the surface and observing reflected light from the surface. No smearing was observed at 100 and 250 mg/sq ft. Slight smearing was observed at 500 mg/sq ft. Smearing was considerable at 1000 mg/sq ft and at 2500 mg/sq ft, it was possible to push the oil on the surface.

#### Safe Concentration Level

From Figures 10 through 12, it would seem that a hexadecane level of 1000 mg/sq ft can be tolerated for gaseous oxygen and a slightly lower level than 1000 mg/sq ft can be tolerated for liquid oxygen. Flaking of

the lubricant in LOX, and film flow at ambient temperature, reduce the safe level to about 500 mg/sq ft.

In liquid oxygen, floating frozen oil will flow with the LOX and accumulate at dead ends downstream. In gaseous oxygen, flowing films will collect at low levels. Sampling of lines for lubricant contaminants should therefore be made at the lowest levels in ambient temperature lines, and at low velocity zones in liquid oxygen systems.

The recommended safe level contamination with hydrocarbons with viscosity and vapor pressure similar to hexadecane is 100 mg/sq ft.

### FILTRATION OF SOLID CARBON DIOXIDE FROM LIQUID OXYGEN

#### General

The average carbon dioxide (CO<sub>2</sub>) concentration in the atmosphere is approximately 320 ppm. In the commercial low temperature air separation processes by which liquid oxygen is produced in the United States, this is reduced to a concentration of the order of 1 to 5 ppm by one of two methods: by scrubbing the air with a caustic solution which combines with the CO<sub>2</sub> to form an insoluble carbonate; by solidification and subsequent filtration. In either case, because of the solubility of CO<sub>2</sub> in liquid air, essentially all CO<sub>2</sub> which enters the cold section of the liquid oxygen producing equipment becomes concentrated in the liquid phase. During the processing of this liquid, it is passed through mechanical filters which are designed to remove the last traces of solid CO<sub>2</sub>. However, it has been the experience of these vendors that not all of the CO<sub>2</sub> is retained by the filters and some is withdrawn in the product.

Few users of commercial oxygen are concerned about the presence of small quantities of solid carbon dioxide. In fact, few commercial users apply liquid oxygen directly. In most cases, the liquid oxygen is vaporized and super-heated to ambient temperatures in the facilities supplied by the customer or vendor. Under these conditions, the solid CO<sub>2</sub> is also vaporized and becomes an unnoticeable contaminant in the usable gas. The storage and rapid turnover characteristics of commercial users preclude concentration of solid CO<sub>2</sub> over periods of weeks to years.

The missile industry alone is faced with the problems of long-term liquid

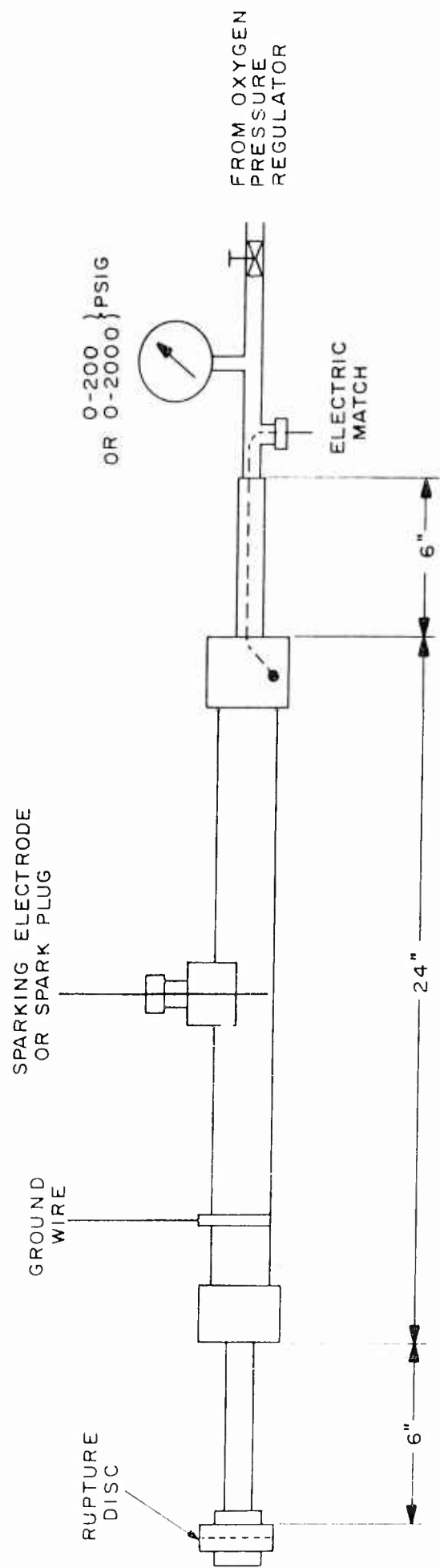


FIGURE 7. SCHEMATIC DRAWING OF APPARATUS USING GASEOUS OXYGEN

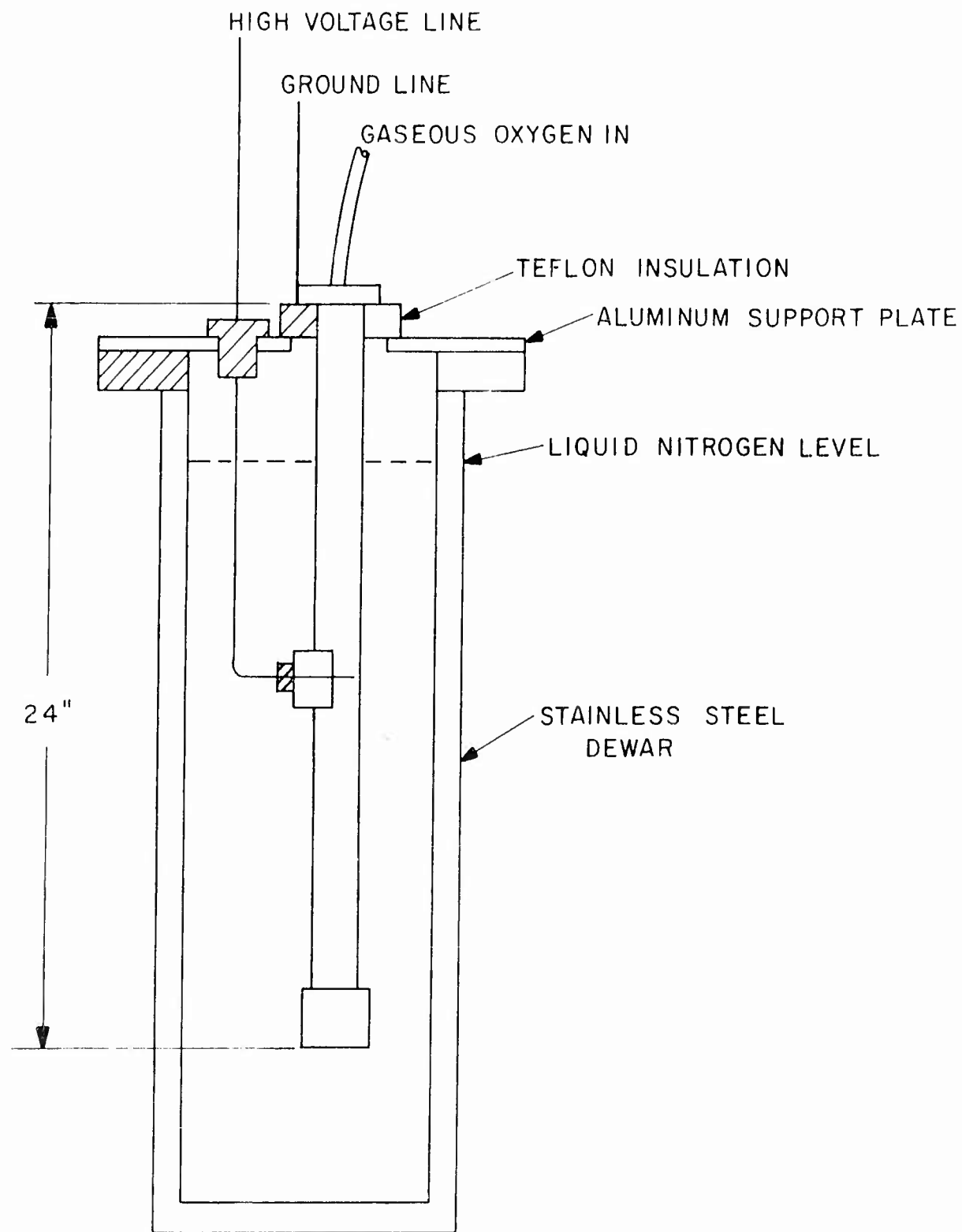


FIGURE 8. SCHEMATIC DRAWING OF APPARATUS  
USING LIQUID OXYGEN

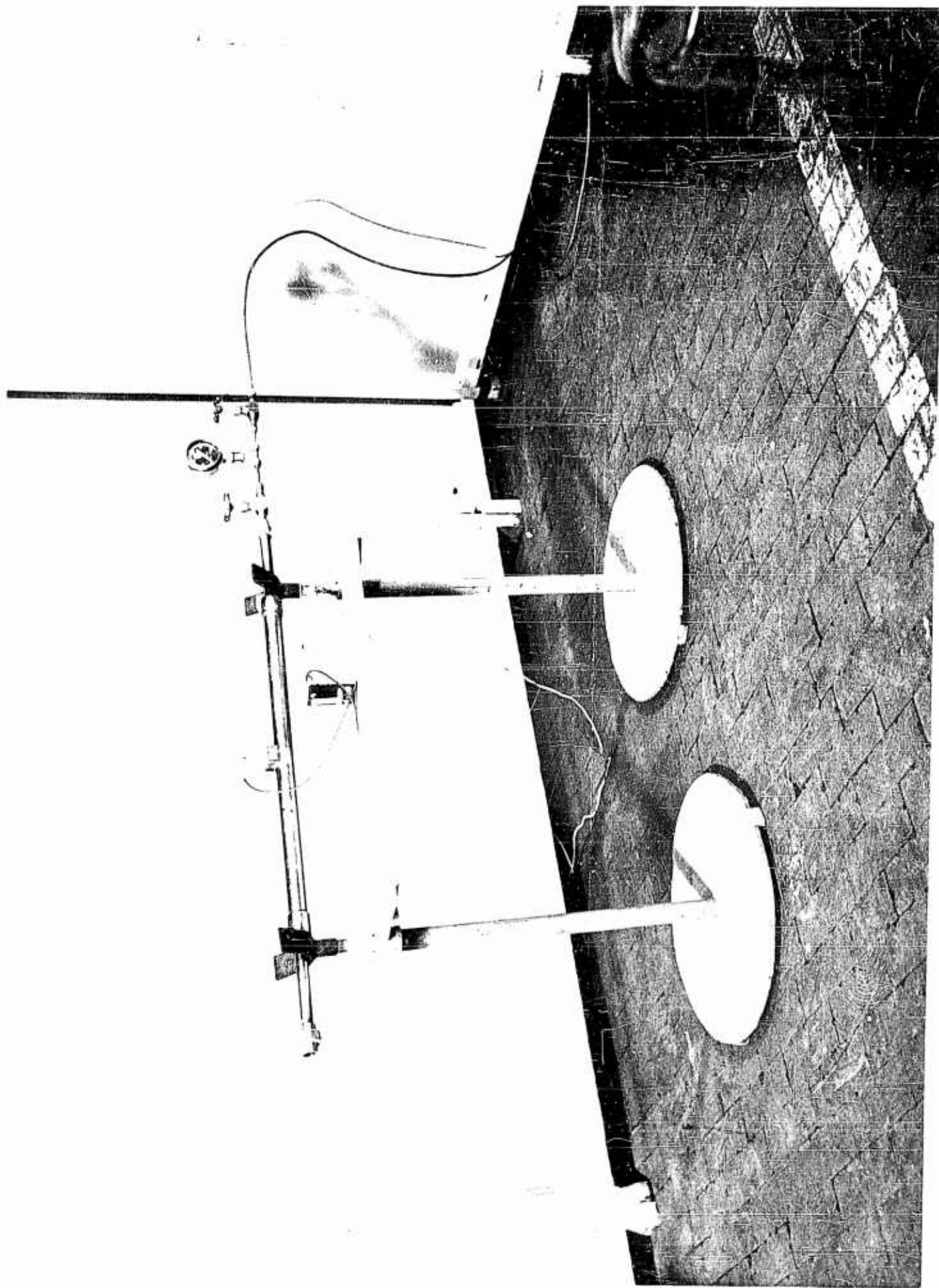


Figure 9. Film Ignition Equipment

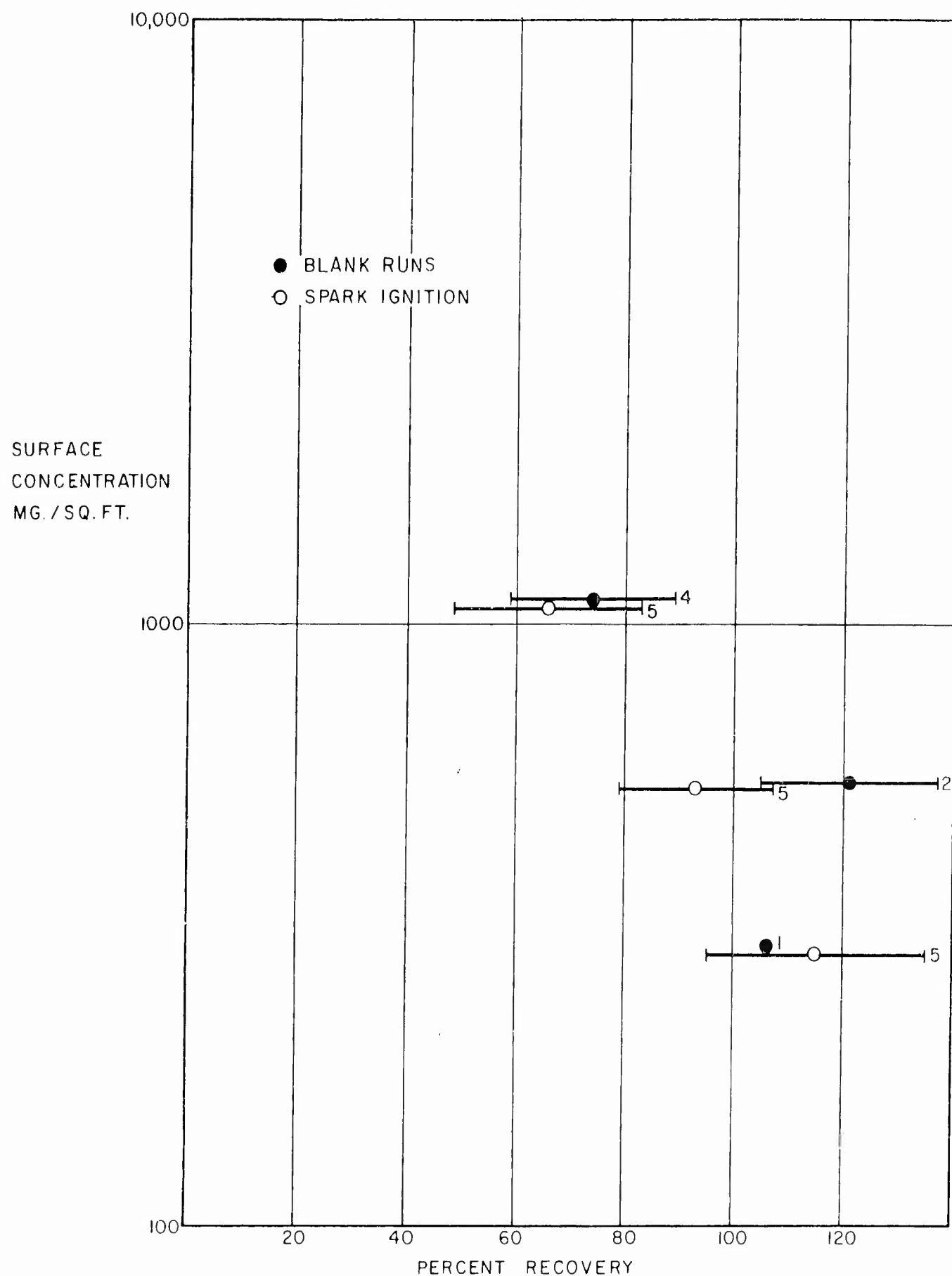


FIGURE 10. RECOVERY OF HEXADECANE FILMS AFTER SPARK IGNITION IN LIQUID OXYGEN

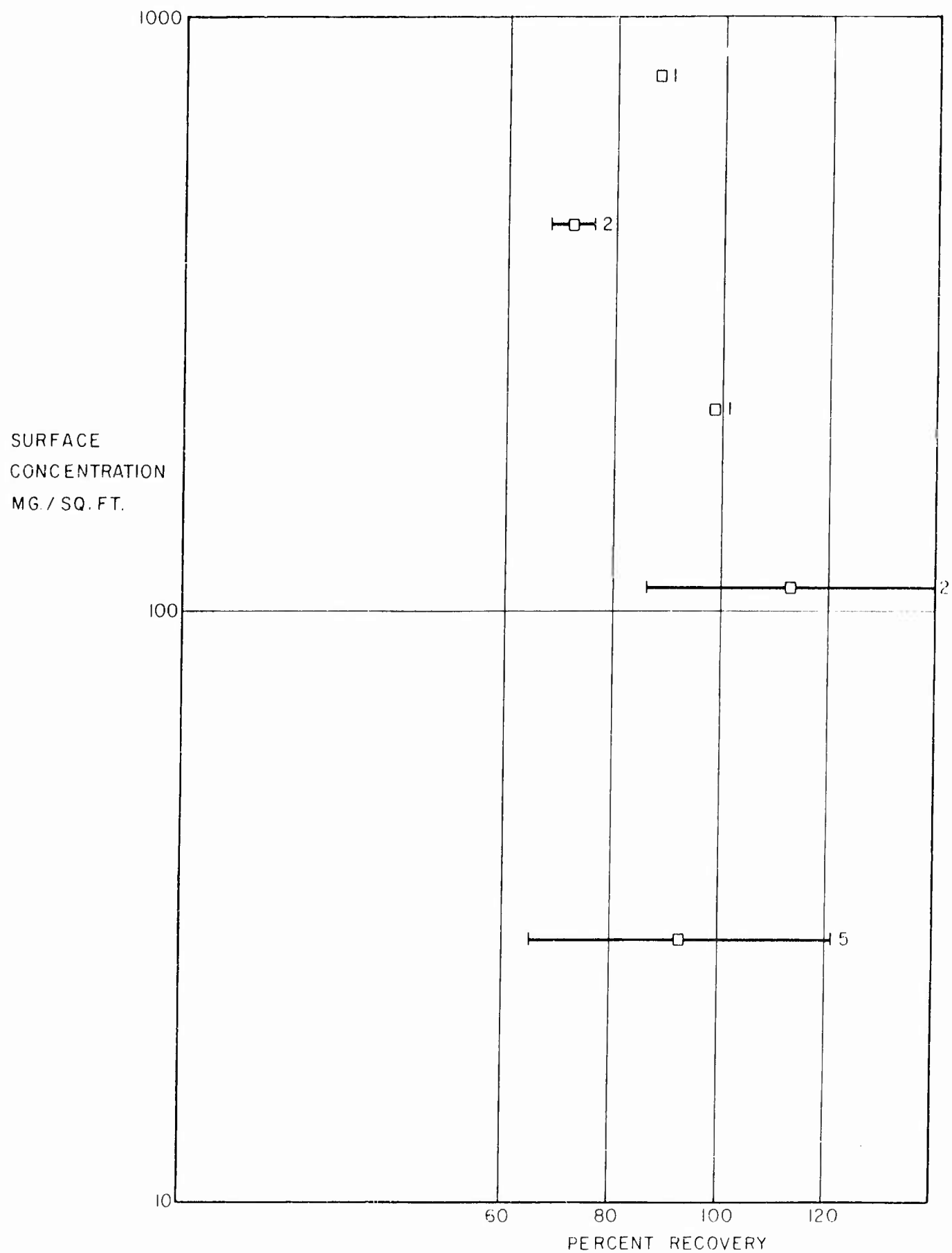


FIGURE II. RECOVERY OF HEXADECANE FILMS AFTER  
IGNITION WITH AN ELECTRIC MATCH IN GASEOUS  
OXYGEN UNDER 200 PSIG PRESSURE

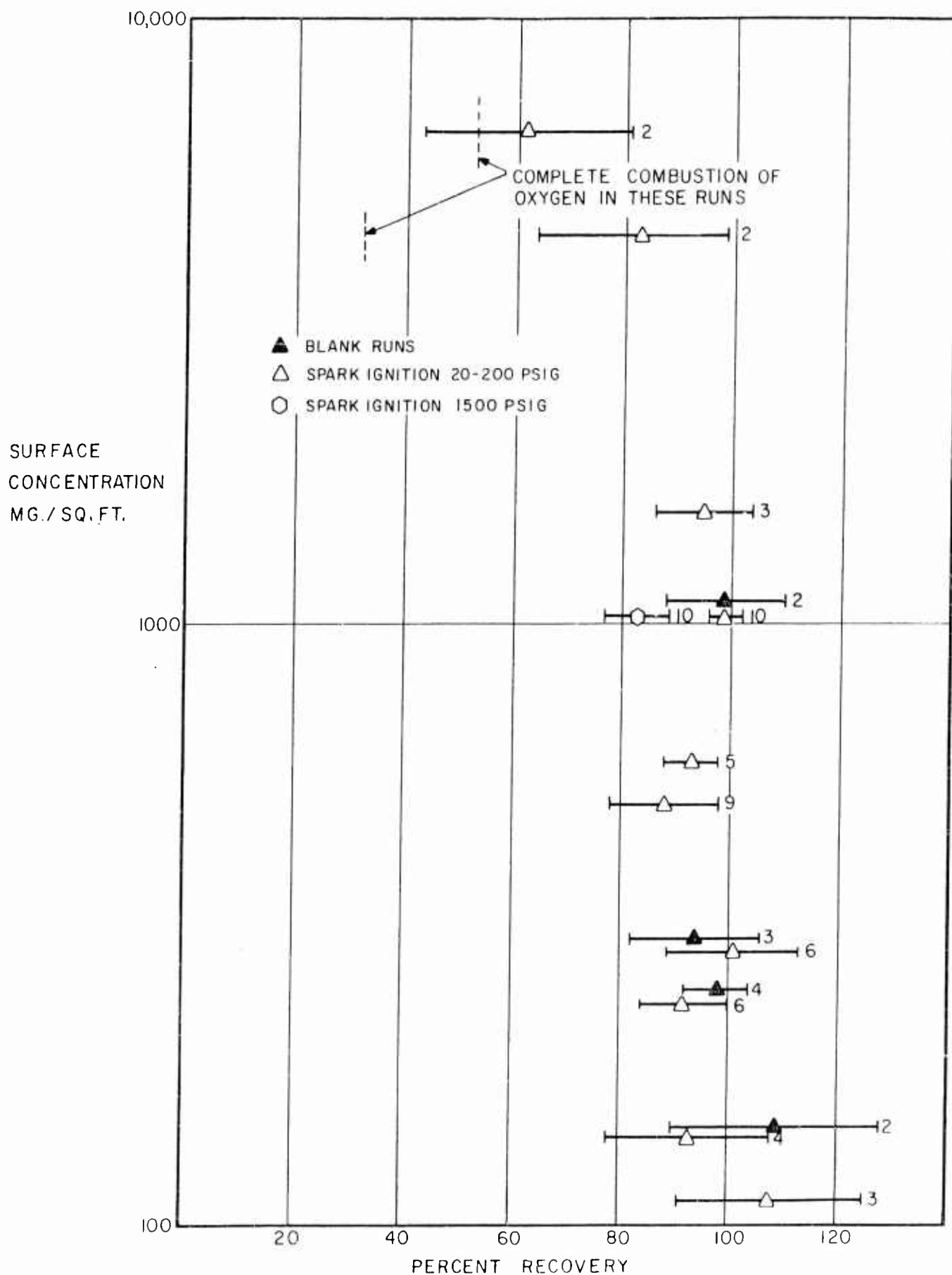


FIGURE 12. RECOVERY OF HEXADECANE FILMS AFTER SPARK IGNITION IN GASEOUS OXYGEN

TABLE VII.  
RECOVERY OF N-HEXADECANE FROM IGNITION TESTS

Surface Concentration mg./sq. ft.	Oxygen Phase	Pressure psig	Igniter	No. of Runs	Recovery Percent	95% Confidence Level for Recovery
145	Gas	50	Blank	2	100, 119	109 ± 19
240	Gas	50	Blank	4	100, 93, 93, 106	98 ± 6
290	Gas	50	Blank	3	103, 82, 97	94 ± 12
1050	Gas	50	Blank	2	94, 105	99 ± 11
110	Gas	200	Spark	2	93, 108	108 ± 17
110	Gas	50	Spark	1	123	---
145	Gas	50	Spark	4	80, 111, 80, 100	93 ± 15
240	Gas	50	Spark	6	86, 92, 102, 83, 89, 103	92 ± 8
290	Gas	50	Spark	6	122, 90, 112, 86, 89, 109	101 ± 12
500	Gas	200	Spark	3	82, 85, 97	88 ± 10
500	Gas	50	Spark	6	86, 64, 77, 91, 95, 116	---
580	Gas	50	Spark	5	93, 85, 100, 92, 97	93 ± 5
1050	Gas	200	Spark	1	83	99 ± 3
1050	Gas	100	Spark	2	100.5, 101.5	---
1050	Gas	50	Spark	5	96, 97, 100, 106, 106	---
1050	Gas	20	Spark	2	98, 99	---
1050	Gas	1500	Spark	10	Original data not available	83 ± 6
1520	Gas	50	Spark	3	88, 93, 103	95 ± 9
4400	Gas	50	Spark	2	74, 92	83 ± 18
6500	Gas	50	Spark	2	53, 72	62 ± 19
28	Gas	200	Electric Match	5	61, 70, 84, 108, 143	93 ± 28
110	Gas	200	Electric Match	2	99, 127	113 ± 28
220	Gas	200	Electric Match	1	99	---

TABLE VII. (Cont'd)

Surface Concentration mg sq ft.	Oxygen Phase	Pressure psig	Igniter	No. Runs	Recovery Percent	95% Confidence Level for Recovery
450	Gas	200	Electric Match	2	70, 74	72 ± 4
800	Gas	200	Electric Match	1	88	-----
274	Liquid	-	Blank	1	106	-----
534	Liquid	-	Blank	2	113, 129	-----
1096	Liquid	-	Blank	4	76, 61, 94, 63	121 ± 16
274	Liquid	-	Spark	5	128, 143, 101, 120, 85	74 ± 15
534	Liquid	-	Spark	4	72, 81, 99, 113, 99	115 ± 20
1096	Liquid	-	Spark	5	85, 55, 48, 54, 39	93 ± 14
						66 ± 17

oxygen storage, concentration of CO<sub>2</sub> by vaporization, and by frequent handlings between vendor, tank truck, launch site storage, and return from missile. Therefore, the relatively new and unexplored field of removal of the last vestiges of solid CO<sub>2</sub> which do remain in the commercial oxygen product part has become of greater importance. The reason is that the solid CO<sub>2</sub> will agglomerate where conditions are static, as found in storage vessel and in the launch pad storage tank. These larger particles may not be broken down during subsequent agitation and may possibly create a blockage in some missile LOX system.

Under the subject contract an investigation was undertaken to study the means and problems of removing the last remaining solid CO<sub>2</sub>. This problem can be divided into two phases: the removal of solid CO<sub>2</sub> from liquid oxygen at the producer's plant site upon or before delivery to the customer, and subsequent removal of CO<sub>2</sub> which may have been in solution in the liquid oxygen as produced by the vendor, but which by reason of handling, long term storage, or involvement in missile operations has been concentrated to the point where the CO<sub>2</sub> has exceeded the solubility limit in liquid oxygen and has begun to precipitate. At this point, the mechanical considerations are given essentially the same as those at the producers' sites. The obvious means of removing solid particles from a liquid is by filtration. In this process the solid-bearing liquid is passed through a medium which contains openings smaller than the smallest desired particles to be left remaining in the solution. These particles are retained on the upstream side of the filter element and at intervals the particles are removed.

This leads directly into a study of the factors involved in satisfactorily filtering solid CO<sub>2</sub> from liquid oxygen. The agglomeration of these particles previous to filtering is of prime importance. This operation is best carried out in a quiescent pool of liquid since turbulence of the mixture tends to break up the particles of solid CO<sub>2</sub>. The factor of particle break-up has been seen to operate on relatively large particles already formed. Although these particles appear to be solid, they break into many small pieces upon agitation of the liquid.

Complicating this situation is the nature of CO<sub>2</sub> particles. These particles cannot be analyzed by the normal screening procedures because of this break-up tendency and because the CO<sub>2</sub> particles exist only at low temper-

atures and not at room temperatures where normal screening processes are conducted. Under approximately 40 microns in diameter, a particle is not visible to the naked eye. Although the filtrate may appear clear, this same liquid, vaporized and heated to room temperature and passed through a CO<sub>2</sub> analyzer, will reveal the presence of CO<sub>2</sub>.

#### Apparatus and Test Procedure

Figure 13 presents a schematic flow diagram of the equipment used in the tests. The equipment is also shown in detail in Figures 14 through 18. This diagram is referenced in subsection - Test Procedure. During a test run, CO<sub>2</sub>-contaminated liquid oxygen is transferred from vessel 1 through Filter 4 and sample coil 5 to vent through V<sub>6</sub>. In order to take a sample, valves V<sub>6</sub> and V<sub>2</sub> are closed, V<sub>7</sub> is opened and the liquid is transferred into the sample bottle 2 where it is vaporized for analysis. Figure 14 shows the equipment in operating position without the Dewars in place.

The identifying numbers on the succeeding photographs are as shown in Figure 13. After 5 runs, filter house (4) was replaced with a Lucite plastic unit so that the filtering process could be visually inspected. Sight glass and scale (6) were used to measure throughput during a test by the liquid level difference.

Figure 15 shows a second generation plastic filter house in a close-up view. The operation of this model is the same as the previous one with exception of the side outlet in the center of the photograph. During the test, the flow enters at the opening at the bottom of the photograph and is split in the filter house. The excess liquid which measures the turbulence leaves by the side opening while the filtered liquid leaves by the connection at the top.

Figure 16 shows the assembly in Figure 15 disassembled for examination. The filter is a 10-micron nominal pore size sintered stainless steel unit purchased as a laboratory item from the Purolator Company. It is approximately 1-1/4" long by 9/16" O.D. Teflon gaskets are used to seal the flange joint. The flow through this filter is from outside to inward.

Figures 17 and 18 schematically show the principle of operation of the test filter unit.

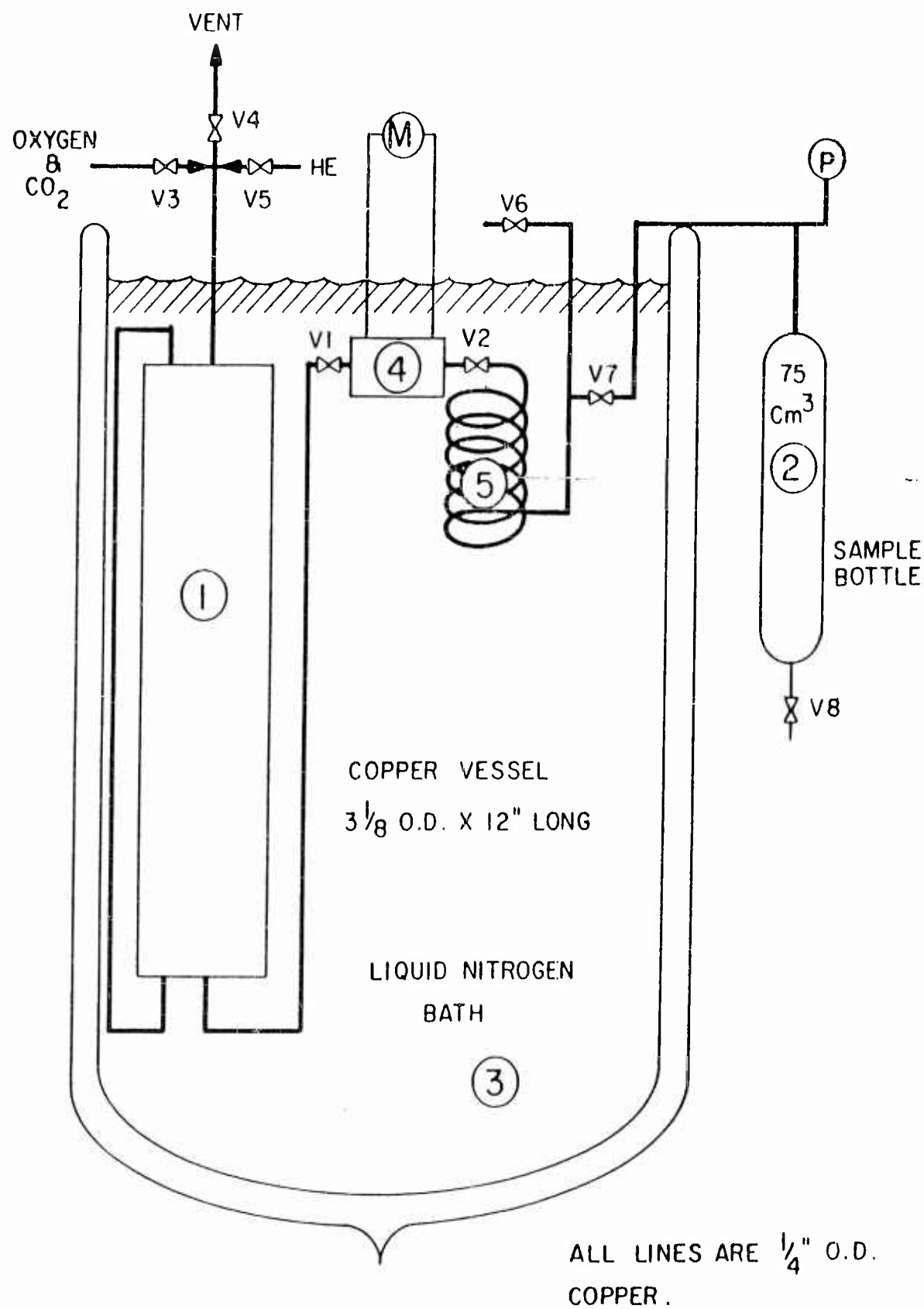


Figure 13.

APPARATUS FOR EXAMINATION OF SOLID  
CO<sub>2</sub> FILTERING PHENOMENON

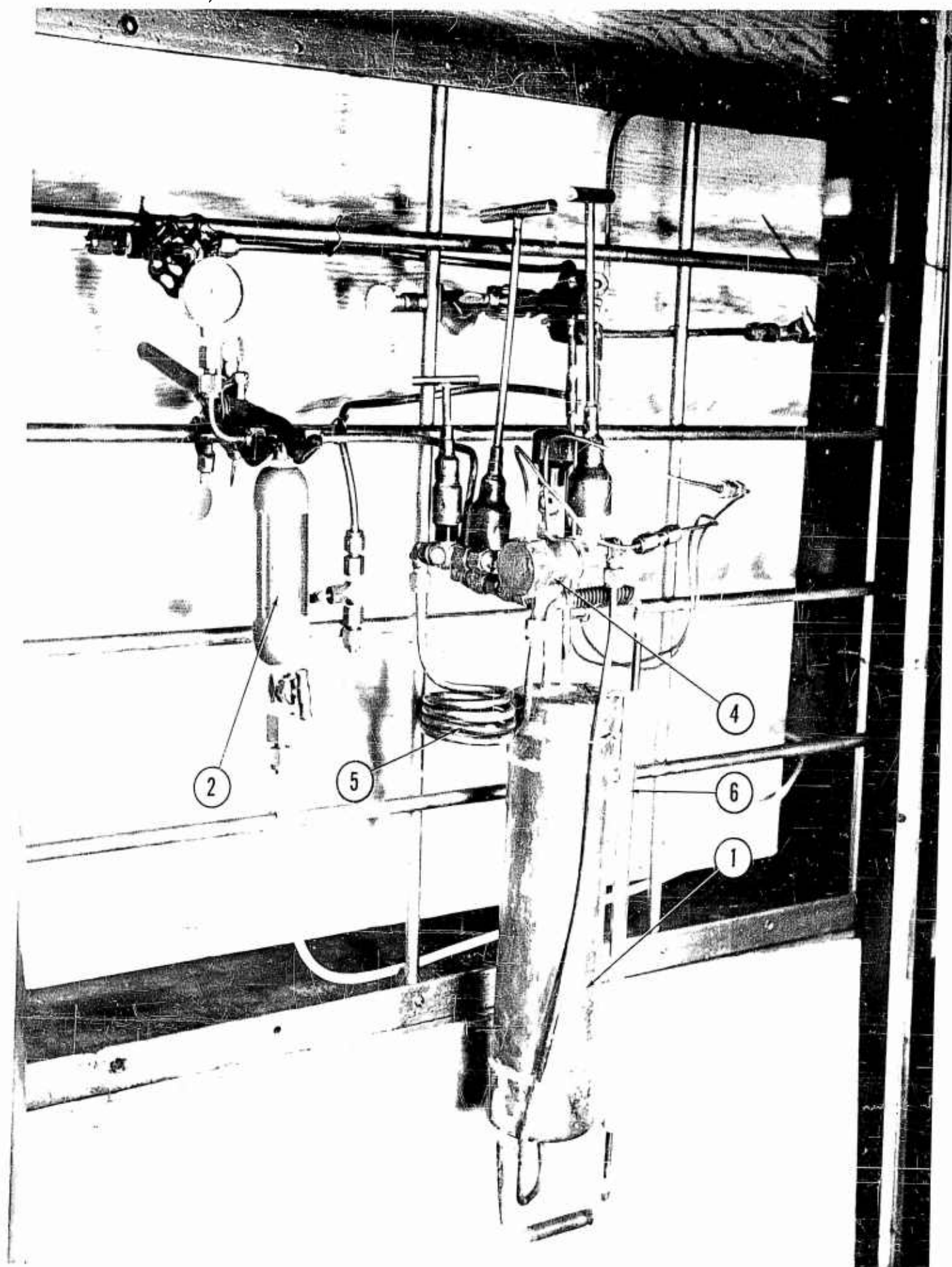


Figure 14. Equipment for Examination of the CO<sub>2</sub> Filtration Equipment

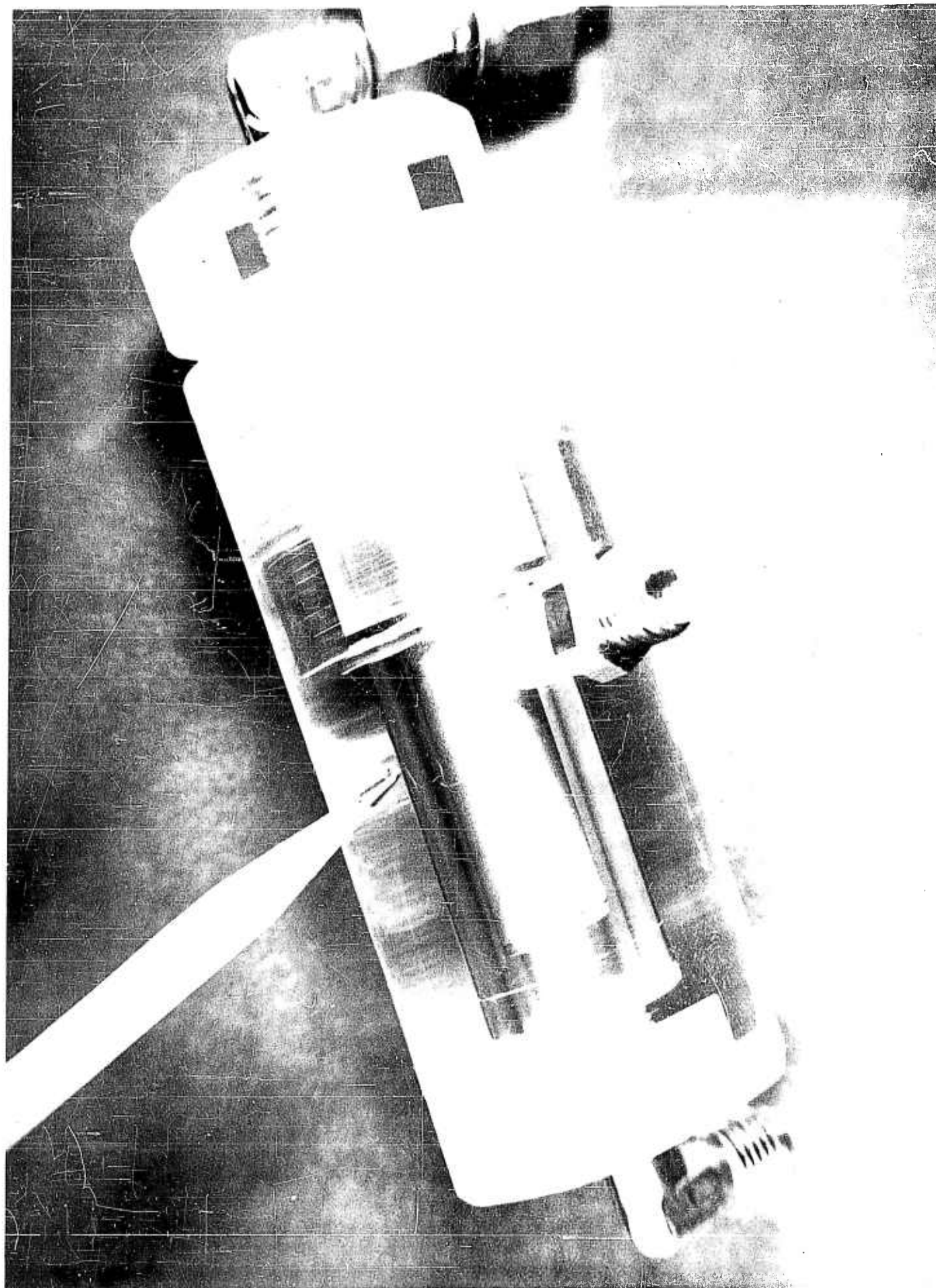


Figure 15. New Filter Assembly with Side Tap

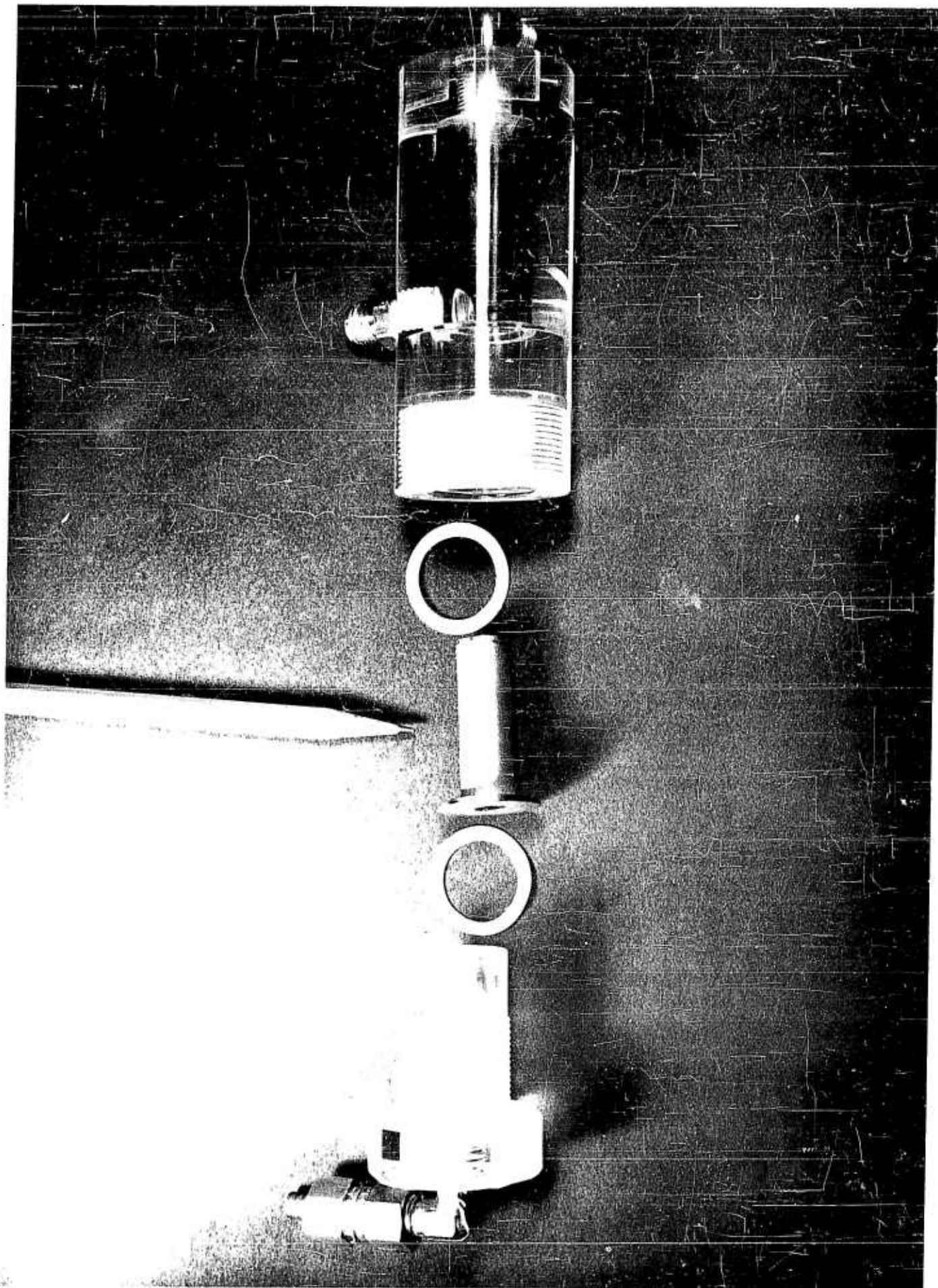


Figure 16. Dissassembled Filter

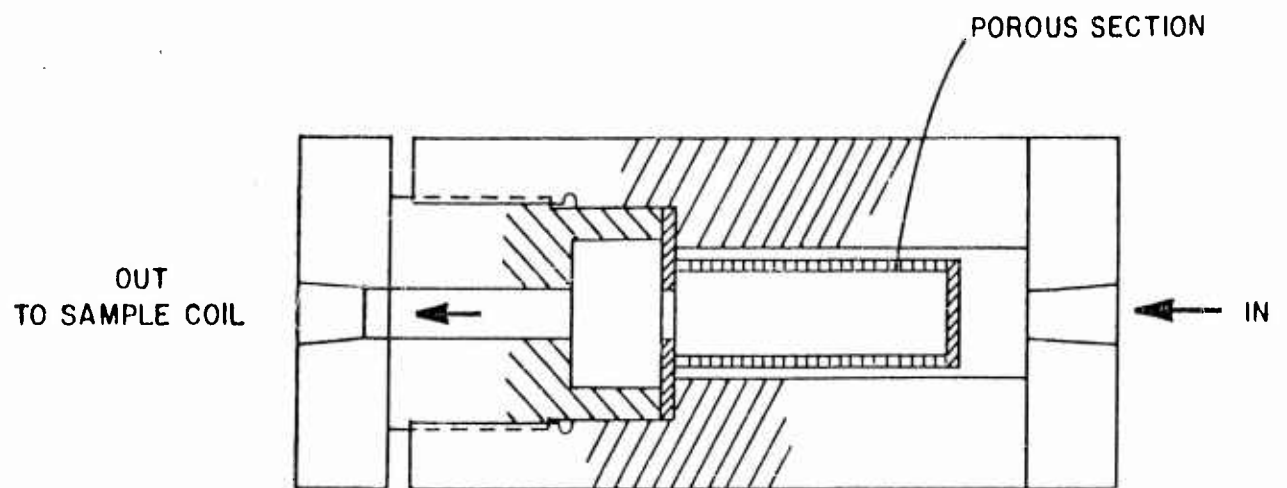


Figure 17  
PLASTIC FILTER ASSEMBLY WITH CYLINDRICAL  
FILTER ELEMENT. (FULL SIZE)

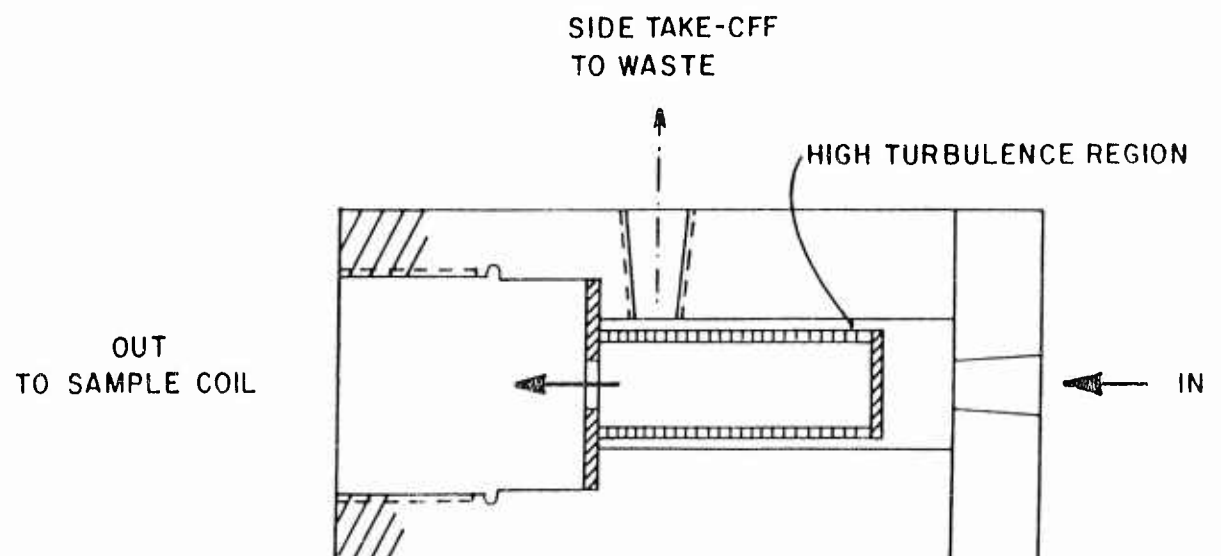


Figure 18  
FILTER ASSEMBLY AS MODIFIED WITH  
SIDE TAKE-OFF FOR HIGH REYNOLDS  
NUMBER. (FULL SIZE)

### Test Procedure

The Dewar flask (3) is first filled with liquid nitrogen. Valve V3 is opened, allowing liquefaction of oxygen containing a known concentration of solid CO<sub>2</sub> into vessel (2). A regulated supply of helium is then connected into the system through valve V5 to apply a steady pressure on the liquid oxygen in vessel A to establish the flowrate through the filter assembly. After steady transfer conditions have been obtained, valves V6 and V2 are closed (V7 had been closed), trapping a sample filter liquid in the sample coil. Valve V7 is opened and the sample is transferred to vessel B by warming the coil to room temperature and cooling vessel B in liquid nitrogen. Valve V7 is closed; the sample bottle is detached, warmed, and analyzed for CO<sub>2</sub>. This procedure is used with all samples where subcooled liquid is filtered.

The same arrangement of the test apparatus is used when boiling liquid is filtered, except a small heat exchanger is inserted immediately before valve V1. This exchanger introduces heat into the contaminated liquid oxygen to the point that approximately 50% gas volume can be observed in the filter house during the filtering procedure. All other parts of the procedure remain the same.

For the runs where a high flow rate was attempted, the 3-1/8" O.D. storage vessel was changed to one 6-1/8" O.D.; the larger storage volume was required in order to make a run for a reasonable time period.

Operation of small-scale equipment for handling liquid oxygen, or any other liquid with a boiling point far below ambient temperature is very delicate. The liquid exhibits a natural tendency to boil at the most inopportune times. The simple operation of throttling the liquid to control flow creates a two-phase system due to flash-off caused by the expansion through a valve. The equipment and procedures for these tests were revised several times.

The procedure of obtaining representative samples from a liquid oxygen stream carrying suspended solid CO<sub>2</sub> is another critical operation. If sampling is done by a simple tap into the stream, the solids will flow past rather than into the side arm which produces a low value. Unless the CO<sub>2</sub>-bearing liquid oxygen is flash-vaporized in a heater whose surfaces are warmer than the sublimation point of CO<sub>2</sub>, the CO<sub>2</sub> will con-

concentrate in the boiling liquid and the resultant analysis will be low. If the tubing carrying the mixture passes through a warm area, the CO<sub>2</sub> will tend to deposit out on the walls of the tube. If the sample is throttled, the CO<sub>2</sub> will tend to deposit out on the valve seal or disc. This difficulty in properly sampling from solid CO<sub>2</sub>-liquid created many problems in test equipment design before productive experimental work could be initiated.

### Discussion of Results

Under this program, 87 separate runs were made under many different conditions using the equipment illustrated. Results of these runs were previously reported. Two phenomena have begun to show even though there is considerable spread in the recorded data due to difficulties in handling the O<sub>2</sub>-CO<sub>2</sub> mixture in small equipment. One difficulty is the passage of visible CO<sub>2</sub> from the exit of the filter element during and immediately after times when the elements have been vibrated mechanically. The filter element was one having 10-micron rating. Since the lower limit of visibility is about 40 microns in diameter, we must assume that this cloud is due to a large quantity of individually invisible particles. It has become apparent during this experiment that the actual filtering medium is the cake which is being built up on the outside of the filter element rather than the filter element itself. In other words, the filter element is simply forming a base for the actual filtering medium. Upon agitation, the CO<sub>2</sub> cake is broken up into smaller particles. Some particles immediately pass through the filter element. Obviously, in a plant with moving machinery such a condition may exist at all times in the actual production filter house.

The second phenomenon is that the concentration of CO<sub>2</sub> in the filtrate seems to vary in a pattern with the Reynolds number of the liquid in the filter house at the surface of the filter cake. Figure 19 represents the results of all runs plotted on one chart, with a proposed correlation of these points. The Reynolds number is a flow correlation of

$$Re = \frac{4w D_h}{A \mu}$$

where:  $w$  = Flow rate, lb/hr  
 $D_h$  = hydraulic diameter, feet  
 $A$  = crosssectional area, sq ft  
 $\mu$  = viscosity, lb/ft sec

As stated previously in this report, the CO<sub>2</sub> particles will agglomerate if the liquid is allowed to stand quietly for a period of time. These agglomerations are known to break up if the quiescent pool is agitated by mechanical means or simply by boiling the liquid. This agitation also occurs during the transfer and filtration of the liquid in the test apparatus. With sufficient agitation, the filtering efficiency of the unit is poor regardless of the rate of flow (See Figure 19).

Figure 20 incorporates data gathered at APCI's Denver Facility in February and April 1960 (3). These data are byproducts of CO<sub>2</sub> sampling tests conducted on the 75 ton per day liquid oxygen generating plant at that location. The data from these tests as shown on Figure 26 agree well with the laboratory scale work in the portion of the curve where over-lapping exists. The extension beyond a Reynolds Number of 10<sup>3</sup> also follows the pattern set up in Figure 19.

It may be readily seen from the foregoing data that filtration of the quality required to completely remove solid CO<sub>2</sub> from the liquid oxygen as it enters the missile tank cannot be accomplished. The liquid oxygen being pumped to the missile is extremely turbulent as it passes through warm lines and fittings to the missile tank. Much of the solid particles are undoubtedly passed through the filter and into the missile tank. While filtration could be accomplished by installing a 1 micron pore size filter, the resultant pressure drop or flow decrease would materially change tanking procedures. In addition, a filter of this fineness is not required for removal of other solid contaminants.

Going one step further, it must be pointed out that even complete filtering (0 ppm solids transferred) is not the full answer to the problem of solid CO<sub>2</sub> in the missile liquid oxygen system. CO<sub>2</sub> is soluble in liquid oxygen to about 4.3 ppm. Upon vaporization of the oxygen during transport through warm lines into a warm missile tank, some of this CO<sub>2</sub> will precipitate. Due to this vaporization the CO<sub>2</sub> concentration will rapidly exceed the solubility limit and precipitate from solution. Thereupon, the status of the liquid becomes comparable to that it would have had there been no serious filtering.

Since, therefore, removal of the CO<sub>2</sub> hazard involves removal of both insoluble and dissolved CO<sub>2</sub>, some process other than in addition to simple filtration is dissolved. Adsorption of the dissolved CO<sub>2</sub> on

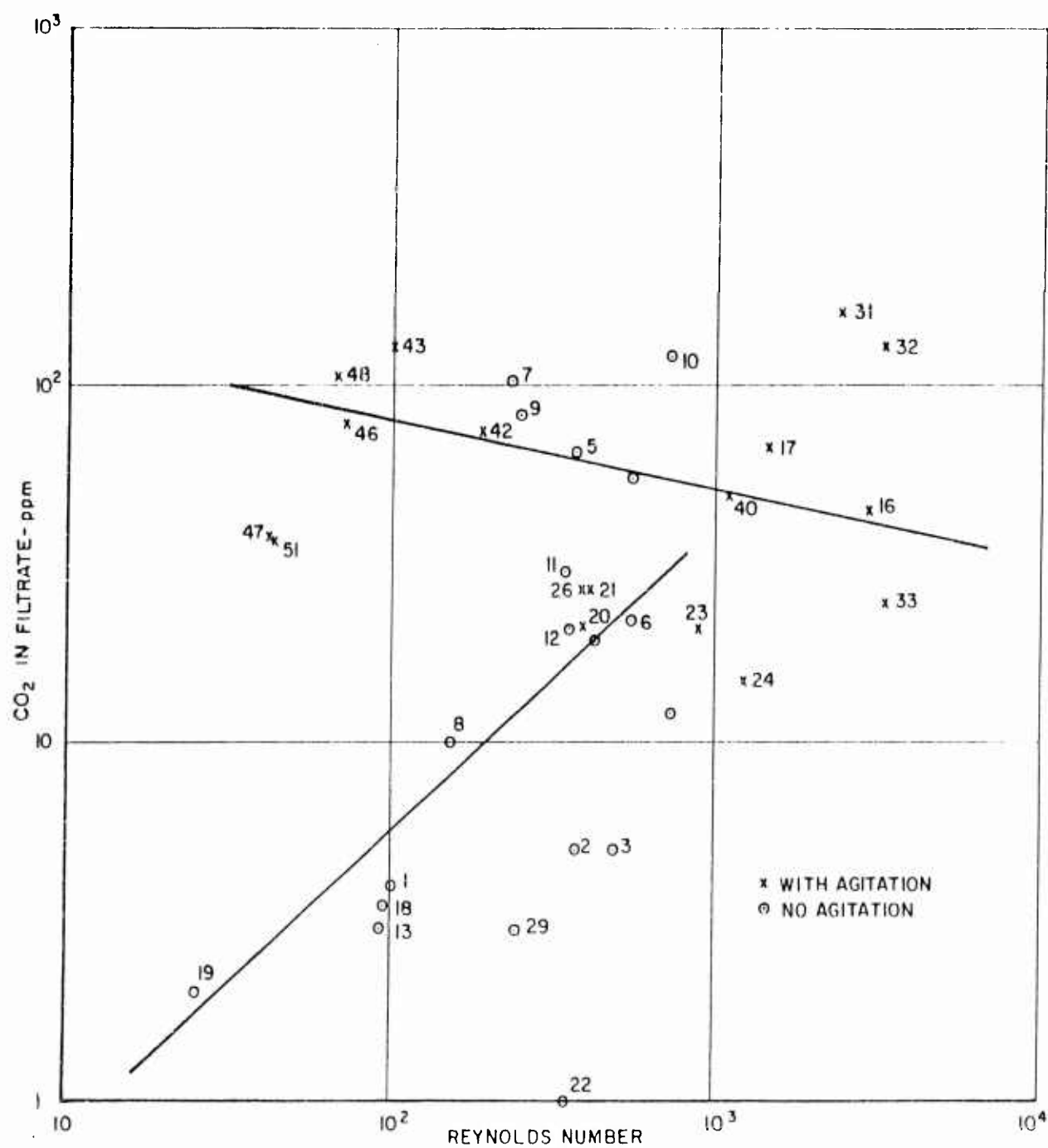


Figure 19  
REYNOLDS NUMBER BEFORE FILTER

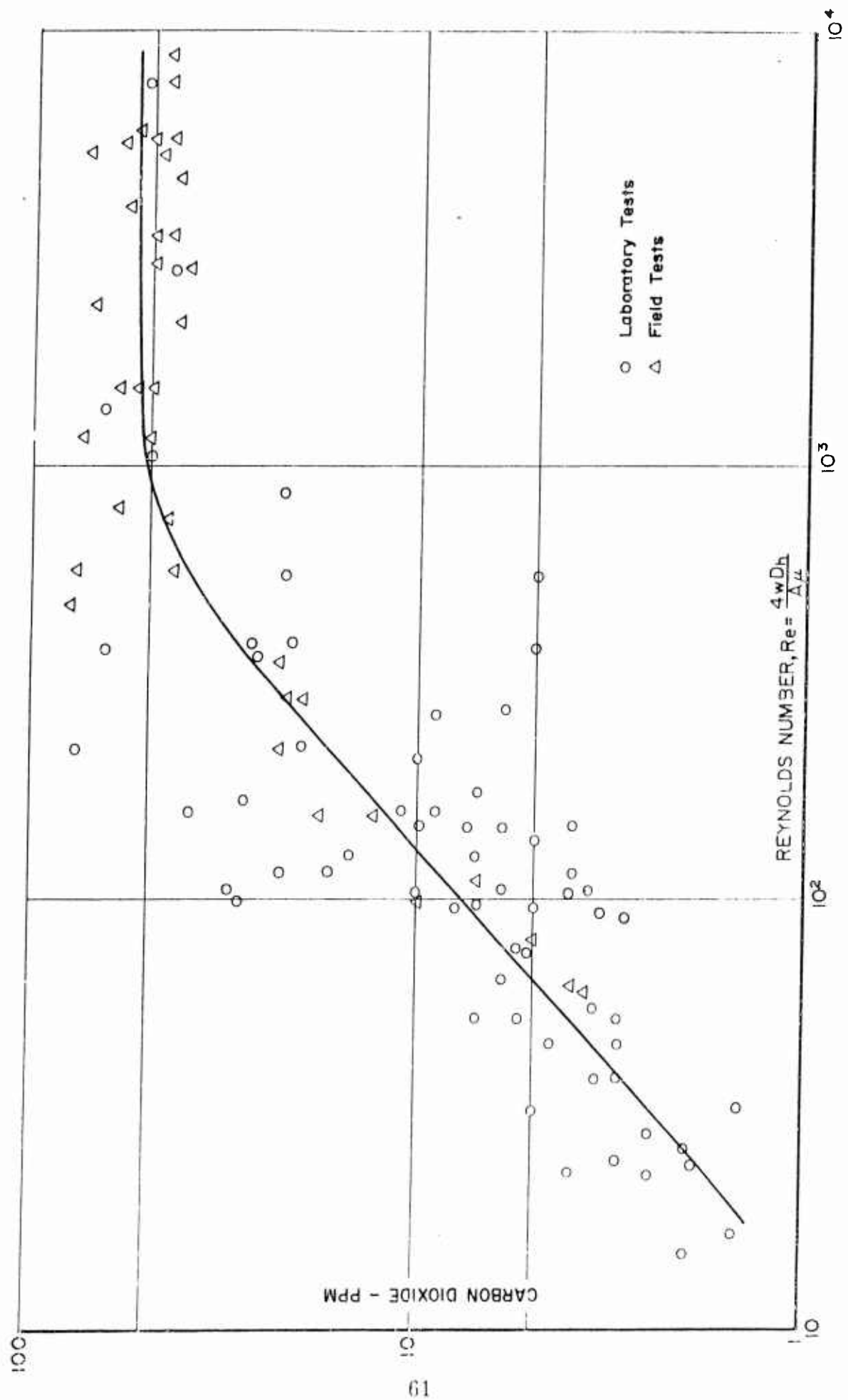


Figure 20. The Variation of Carbon Dioxide After Filtration to Reynolds Number in Filter Assembly.

silica gel or molecular sieve is the most likely solution. However, because of the cost of equipment and the fact that this is another piece of equipment in the already complex ground support phase, the question "Is solid CO<sub>2</sub> in missile liquid oxygen dangerous?" should be answered. No missile failures have been attributed directly to the presence of CO<sub>2</sub> in the system. However, the present test for particulate matter requires warming the sample to atmospheric temperature. During this warm-up period, the CO<sub>2</sub> sublimates (-110° F) and thus is not visible on inspection. Inspections of fill line filters while cold have shown solid water and CO<sub>2</sub> on their surfaces, however.

The filtration of natural inert solids, rust, stones, metal chips, welding slag presents no particular problem. However, little can be done about filtration of these items until the various rocket engine and systems engineers settle on an allowable maximum size particle. It is understood that tests are being run with liquid oxygen and fuel contaminated with increasingly larger particles to determine the practical upper limit for particulate matter sizing.

#### SUPPLEMENTAL AGREEMENT NO. 2

##### LOX Handling Practice - Cape Canaveral

The liquid oxygen used at Cape Canaveral is usually supplied by the LOX production facility operating at the Cape. This facility consists of two independent plants (1160 and 1161), each capable of producing 75 tons (15,700 gal.) of LOX per day, and four plant storage tanks, each with a capacity of 28,000 gallons. Generally, both plants operate at the same time, although during times of low demand, or when the plant storage tanks are full, one plant may operate while the other is either standing by or is being maintained. Occasionally, at times of peak demand, LOX may be brought in from an outside source.

When liquid oxygen is required at one of the complexes, tank trailers are driven to the production facility and loaded with LOX which is filtered as it is pumped from the plant storage tanks. Four trailers may be loaded at one time from the filter manifold, each trailer having a capacity of 3800 gallons. When the trailers are filled, they are driven to the complex area and unloaded into the pad storage tank, which has a capacity of 28,000 gallons. The trailers are unloaded by pressurizing the trailer tank with

oxygen gas and forcing the contents into the pad tank through a portable filter unit.

Activities associated with the LOX storage tanks may consist of launches, static firing tests, incompletes or recycled countdowns, missile tanking tests, dumping the storage tank contents, filling and topping the storage tank, and taking samples for analysis. When a missile is scheduled to be launched, one of the last operations to be performed is loading the missile with LOX. About 30 minutes before the launch, the LOX storage tank is pressurized with nitrogen gas to about 30 psig to provide pump suction head and the liquid oxygen is pumped through filters into the missile tank. The missile tank is kept full by adding subcooled liquid oxygen to compensate for boil-off. If the count is held up after the LOXing operation, the missile tank is topped with LOX until the count is either continued, recycled, or cancelled. If the count is seriously delayed or cancelled, the LOX in the missile tank is either returned to the storage tank or discarded. Static firing tests follow the same procedure as the actual launches. Tanking tests are designed to test the LOX handling system by filling the missile tank. After a tanking test, the LOX in the missile tank may be returned to the storage tank or discarded. After a storage tank is dumped, generally because the LOX does not meet purity or particle count specifications, the tank is usually purged afterward with gaseous nitrogen. When a storage tank is topped, it is generally filled until the LOX overflows from the tank vent line.

#### Experimental Program

Samples of liquid oxygen were taken periodically from the LOX storage tanks of four Atlas complexes (Pads 11, 12, 13, and 14) and two Titan complexes (Pads 19 and 20), as well as from the process stream of the LOX production facility at Cape Canaveral. These samples were then shipped to Air Products, Incorporated (API) at Allentown, Pennsylvania where they were analyzed for a variety of components. At times, duplicate samples were taken by Pan-American Airways Pad Engineering and analyzed at the Patrick AFB Laboratory. In this way, cross-checks were made of the validity of the analytical methods. Analyses at Allentown were performed on all samples by at least two different instruments. The first instrument was a dispersive-type infrared spectrophotometer (Beckman IR-4) which was used to determine carbon dioxide, methane, nitrous oxide, water vapor, and acetylene. The

second instrument was a Multi-Contaminant Analyzer (MCA) developed by Air Products for WADD under Contract No. AF 33(616)-6747 and made available for the present study. This instrument used separate non-dispersive (Luft Principle) infrared optical benches for measuring the various contaminants, and a paramagnetic analyzer for measuring oxygen concentration. The contaminants determined by the MCA were total hydrocarbons (THC), carbon dioxide, carbon monoxide, acetylene, butane plus hydrocarbons, and water. Details of the analytical techniques are described in the Section "Discussion of Sampling and Analyses".

The sampling apparatus and sampling technique used in this study were described in a previous report. The sampling apparatus used is capable of taking true liquid samples provided the sampling period is no longer than ten minutes. In order to cool the sampling lines and sampler quickly enough to stay within the time limit, it was necessary to pressurize the LOX storage tanks to 20 psig with gaseous nitrogen.

This requirement not only introduced additional nitrogen to the bulk of the LOX as a contaminant, but also complicated the taking of a sample since the vent valve and pressurization controls were located in the block-house of the pad.

The samples at the pads were taken from the LOX sampling line normally used to take routine samples. Until the present program, routine sampling had consisted of draining liquid oxygen from the storage tank via the sampling line into an open-mouthed stainless steel vacuum bottle (4). In order to distinguish between samples taken with open flasks and those taken with the closed sampler, the former are called liquid samples and the latter are called cryogenic samples. Duplicate cryogenic samples were taken by splitting the sample stream through a tee connection and filling two identical samplers simultaneously. After a cryogenic sample was taken and the sampler valves were closed, the trapped sample was allowed to warm and vaporize. At ambient temperature, the pressure inside the sampler generally reached about 1000 psig.

No formal sampling schedule was followed, but samples were taken depending on the activities at the pads and the availability of support personnel. Efforts were made to obtain samples before and after particular activities such as missile tanking tests, launches, and storage

tank toppings. It proved impossible, with the equipment available, to obtain successful samples from the trailers used to carry LOX from the production facility to the complexes.

#### History of Activities on Complexes

In order to interpret the data obtained during the course of the study period, it is necessary to consider each pad separately. The following descriptions are intended to provide a general background for each pad without going into much detail on individual samples.

##### Pad 11 - Convair

At the start of the test program, this complex had been inactive for a number of months due to modifications. During this inactive period, the LOX storage tank had been cleaned and inspected, remaining in clean condition until February 2, 1961 when the tank was filled with liquid oxygen. From that date until the completion of the sampling program (March 28), activities concerning the LOX storage tank consisted of one missile tanking test and ten topping loads of LOX added to the storage tank. From February 16 through March 28, eight samples were taken from the tank and subsequently analyzed. Of these eight samples, one was taken one hour after completion of the tanking test, one was taken less than one hour after topping, and one was taken about 14 hours after topping. In the cases of the other five samples, there were no particular activities at the storage tank for at least 16 hours before taking samples.

##### Pad 12 - Convair

After a period of considerable activity, a missile was launched on January 23 and the complex was shut down for modifications. The liquid oxygen which remained in the storage tank after the launch (approximately 11,000 gallons) was allowed to boil away by normal heat leak during the remainder of the test period, reaching a residual level of approximately 1400 gallons on March 29. Five samples were taken at the LOX storage tank during this inactive two-month period. During the active period, one sample was taken on a normal day and one sample was taken seven hours before the launch. The storage tank was topped three times during the active period.

Pad 13 - Convair

This complex was the most active of the six pads studied; four missiles were launched during the course of the study period. This activity is reflected by the 16 LOX tank loadings which occurred during the test period. Altogether, ten samples were taken from the LOX storage tank and analyzed. Of these samples, two were taken about five hours after a tank topping and one was taken about one hour after topping. No storage tank activities took place at least 24 hours before taking any of the other seven samples.

Pad 14 - Convair

Only one missile was launched from this complex during the three-month period. Other activities at the LOX storage tank during this period included one missile tanking test and seven loads of LOX delivered to the storage tank. Also, the contents of the LOX storage tank were discarded once, since the LOX did not meet specifications. A 24-hour purge with nitrogen gas followed the dumping of the LOX. Ten samples were taken during the study period and analyzed. Of the ten samples, two were taken about one hour after topping the storage tank. The other eight were taken at times of no particular activity.

Pad 19 - Martin

This complex was almost as active as Pad 13; three missiles were launched and one static firing test was conducted. The LOX tank was loaded on 12 occasions and nine samples were taken during the course of the study period. Of the nine samples, one was taken about one hour after topping, one was taken about three hours after topping, and one was taken 18 hours after a launch. There was no particular activity at least 24 hours before taking any of the ten other samples.

Pad 20 - Martin

Although more active than Pad 14, this complex was not as active as Pad 19, launching two missiles during the three-month period. Eight loads of LOX were added to the storage tank and eight samples were taken. No particular activities were associated with any of the eight samples.

### LOX Plant

With the exception of some problems associated with mal-functioning of the CO<sub>2</sub> filters and adsorbers in these plants, both plants operated at normal production rates as controlled by the available plant site storage capacity.

### Discussion of Results

The chronology of tank loadings, samples, and special activities during the three-month study period is presented in Table VIII. In this table, the left-hand column under each pad number presents the the individual sample numbers. The center column indicates special activities which are represented by letters; "L" standing for launches, "T" for tanking tests, "D" for dumping LOX, and "S" for static firing. The right-hand column presents LOX tank loadings in thousands of gallons. Under the designation LOX Plant, the left-hand column refers to the sample numbers and the number in parentheses indicates the LOX plant which was sampled.

Three of the 68 samples were completely unsuccessful. The complete analytical data of the 65 analyzed samples were reported previously. For the sake of clarity, the accumulated data have been interpreted and condensed into Table IX. In this table, the CO<sub>2</sub> data were obtained from the multi-contaminant analyzer.

Table X gives the analytical results of the samples which were taken shortly after some activity involving the sampled storage tank had taken place.

Table XI presents the results of all of the duplicate samples which were taken. Sample 59 in Table XI is the single sample which was analyzed by both Air Products and Patrick AFB Laboratories.

### Carbon Dioxide

As can be seen in Table IX of the results, in practically every sample the CO<sub>2</sub> was found to be in quantities well above its solubility limit of 4.2 ppm in liquid oxygen. This indicates that solid CO<sub>2</sub> was sus-

TABLE VIII - CHRONOLOGY OF STORAGE TANK ACTIVITIES

Date	PAD 11			PAD 12			PAD 13			PAD 14			PAD 19			PAD 29		
	Samp. No.	Spec. No.	Load, gal 1000	Samp. No.	Spec. No.	Load, gal 1000	Samp. No.	Spec. No.	Load, gal 1000	Samp. No.	Spec. No.	Load, gal 1000	Samp. No.	Spec. No.	Load, gal 1000	Samp. No.	Spec. No.	Load, gal 1000
1									14.7									
2						29.5												
3				2		5.2									2.3			
4						5.5												
5							3		2.2						0.6			
6										4		16.2						
7													5		22.5			
8									5.4							7		
9									2.9					L				
10				3	L		3											
11								L	14.8	10								
12							12						11		25.3			
13																		
14																		
15																15		4.1
16										16		4.6						
17								D		T						17		
18			21.5	18														

(continued)

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TABLE VIII - CHRONOLOGY OF STORAGE TANK ACTIVITIES  
(continued)

	PAD 11	PAD 12	PAD 13	PAD 14	PAD 19	PAD 20
	Samp. No.	Samp. Spec. No.	Samp. Spec. No.	Samp. Spec. No.	Samp. Spec. No.	Samp. Spec. No.
	Load. gal 1000	Load. gal 1000	Load. gal 1000	Load. gal 1000	Load. gal 1000	Load. gal 1000
3 7			9.7	42		
3 8		44				
3 9	45 (1161)					
3 10	6.6					
3 11			3.4			
3 12			32.6			
3 13			L	47		
3 14	48				49	50
3 15						
3 16	51		25.9			
3 17		54				
3 18						
3 19	5.4			55		15.2
3 20			32.9			
3 21	57				60	
3 22						
3 23						
3 24					1.5	
3 25			L(?)			
3 26						
3 27	1.5					
3 28						
3 29	63		26.1	10.8	61	
3 30		65		68		67
3 31	56 (1161)					
3 32						

TABLE IX

## SUMMARY OF ANALYTICAL RESULTS

Location (Pad or Plant)	Date Sampled	Sample	CO <sub>2</sub> (ppm)	THC (ppm)	CH <sub>4</sub> (ppm)	C <sub>2</sub> H <sub>2</sub> (ppm)	C <sub>4</sub> + (ppm)	Purity (Mol %)	LOX Volume (gallons)
11	2/16	1	17	14	15	-	-	99.75	F *
11	2/23	2	39	17	17	-	-	99.78	F
11	3/6	3	25	20	22	-	-	99.55	26,500
11	3/13	4	11	16	15	trace	-	99.45	F
11	3/15	5	10	16	16	-	-	99.53	F
11	3/16	6	15	22	19	-	-	99.45	F
11	3/20	7	10	17	16	-	-	99.35	F
11	3/28	8	12	20	20	-	-	99.45	F
12	1/10	1	14	13	18	-	-	99.70	-
12	1/23	2	13	20	17	-	-	99.40	F
12	2/2	3	8	13	15	-	-	98.95	8,500
12	2/16	4	14	18	21	-	-	99.45	4,600
12	3/8	5	11	24	27	-	-	99.73	2,200
12	3/16	6	7	31	31	-	-	99.73	2,100
12	3/29	7	10	43	45	-	-	99.60	1,400

\* (F denotes Full Tank)

TABLE IX (Cont'd)

Location (Pad or Plant)	Date Sampled	Sample	CO <sub>2</sub> (ppm)	THC (ppm)	CH <sub>4</sub> (ppm)	C <sub>2</sub> H <sub>2</sub> (ppm)	C <sub>4</sub> <sup>+</sup> (ppm)	Purity (Mol %)	LOX Volume (gallons)
13	1/16	1	13	16	17	-	-	99.30	F
13	1/23	2	14	19	18	-	-	99.30	F
13	1/26	3	15	19	16	-	-	99.40	Low
13	2/9	4	9	16	14	-	-	99.40	22,700
13	2/14	5	11	16	15	-	-	99.40	22,300
13	2/20	6	43	16	16	-	-	99.50	22,000
13	2/27	7	15	15	16	-	-	98.40	5,000
13	3/8	8	17	14	16	trace	-	99.50	F
13	3/15	9	25	21	23	-	-	99.77	F
13	3/20	10	13	14	15	-	-	99.75	F
14	1/17	1	24	54	30	-	-	99.40	--
14	1/25	2	35	32	25	-	-	99.60	F
14	2/1	3	14	19	21	-	-	99.60	F
14	2/9	4	22	22	20	-	-	99.60	21,800
14	2/17	5	15	16	15	-	-	99.70	F
14	2/28	6	14	17	17	-	-	99.50	5,000
14	3/7	7	20	16	16	trace	-	99.70	23,000
14	3/13	8	14	16	16	trace	-	99.60	21,500
14	3/17	9	20	20	20	trace	-	99.60	20,500
14	3/24	10	11	17	15	-	-	99.70	F

TABLE IX (Cont'd)

Location (Pad or Plant)	Date Sampled	Sample	CO <sub>2</sub> (ppm)	THC (ppm)	CH <sub>4</sub> (ppm)	C <sub>2</sub> H <sub>2</sub> (ppm)	C <sub>4</sub> <sup>+</sup> (ppm)	Purity (Mol %)	LOX Volume (gallons)
19	1/18	1	18	24	20	-	-	99.50	F
19	1/25	2	16	15	13	-	-	99.40	F
19	2/3	3	11	13	15	-	-	99.50	27,200
19	2/13	4	11	18	15	-	-	98.60	5,500
19	2/16	5	25	10	13	-	-	98.60	27,800
19	2/21	6	37	19	16	-	-	98.90	10,300
19	3/14	7	12	18	16	0.25	-	99.40	27,200
19	3/21	8	10	19	17	0.13	-	99.50	F
19	3/28	9	12	18	17	0.16	-	99.50	F
20	1/19	1	20	14	18	-	-	99.70	--
20	1/27	2	17	19	17	-	-	99.40	--
20	2/2	3	11	13	13	-	-	99.50	F
20	2/13	4	12	22	18	-	-	98.60	<4,000
20	2/20	5	16	20	20	-	-	98.80	<4,000
20	2/28	6	23	15	16	-	-	98.00	25,000
20	3/14	7	16	17	17	-	-	98.6	7,600
20	3/29	8	17	16	17	-	-	99.50	25,000

TABLE IX (Cont'd)

Location (Pad or Plant)	Date Sampled	Sample	CO <sub>2</sub> (ppm)	THC (ppm)	CH <sub>4</sub> (ppm)	C <sub>2</sub> H <sub>2</sub> (ppm)	C <sub>4</sub> <sup>+</sup> (ppm)	Purity (Mol %)	LOX Volume (gallons)
1160	1/6	1	3	10	11	-	-	99.80	--
1160	1/19	2	61	7	12	-	-	99.70	--
1160	1/27	3	63	7	15	-	-	99.70	--
1161	2/3	4	110	3	11	-	-	99.60	--
1161	2/14	5	74	80	22	-	-	99.70	--
1161	2/17	6	52	16	12	-	-	99.70	--
1160	2/23	7	36	15	14	-	-	99.90	--
1161	2/27	8	>100	15	15	-	-	99.70	--
1161	3/9	9	25	12	13	-	-	99.60	--
1161	3/9	10	24	12	13	-	-	99.60	--
1160	3/15	11	47	13	16	-	-	99.70	--
1160	3/20	12	50	13	14	-	-	99.50	--
1161	3/29	13	10	12	12	-	-	99.60	--

pended in the LOX and was taken as part of the liquid sample. The CO<sub>2</sub> concentrations found in the samples from the complexes were in the range from 10 to 40 ppm with the average around 20 ppm. In contract, the CO<sub>2</sub> found in the samples from the LOX production unit averaged higher than 50 ppm, with a few samples out of the range of the analytical instruments.

The high CO<sub>2</sub> obtained from the LOX production unit can be traced to some extent to damaged filters in both LOX plants. These filters were in the process of being repaired during this program and the success of the repair effort can be seen in the last two samples from the 1161 LOX plant, with CO<sub>2</sub> contents of 9.5 ppm and 24 ppm.

Although the sampling of suspended solids is far from exact, the relative uniformity of the CO<sub>2</sub> analytical results indicate that the suspended solid CO<sub>2</sub> must have been distributed quite uniformly in the bulk of the oxygen liquid. However, it must also be pointed out that the CO<sub>2</sub> results given in Table IX should not be taken as a true measure of the CO<sub>2</sub> inventory, since considerable solid CO<sub>2</sub> probably settled in the tanks. This point is illustrated by Figure 21 where the CO<sub>2</sub> concentration and the residual liquid oxygen volume at Pad 12 are plotted as functions of time. The LOX in this storage tank was allowed to boil away undisturbed for a period of 65 days. Although there was no chance for any significant amount of the original CO<sub>2</sub> to leave the system, the apparent CO<sub>2</sub> concentration hardly changed while the volume of liquid oxygen decreased by a factor of eight. This indicates that the excess solid CO<sub>2</sub> settled to the bottom of the tank.

### Hydrocarbons

The results from the hydrocarbon analyses, which included total hydrocarbons (THC), methane, acetylene, and butane and heavier hydrocarbons (C<sub>4</sub>+), present a picture of relatively uniform and almost insignificant hydrocarbon contamination, both at the LOX plants and at the active pads. With the exception of acetylene, the only other hydrocarbon detected was methane, the least hazardous of the hydrocarbons. There was only a small (approximately 25%)

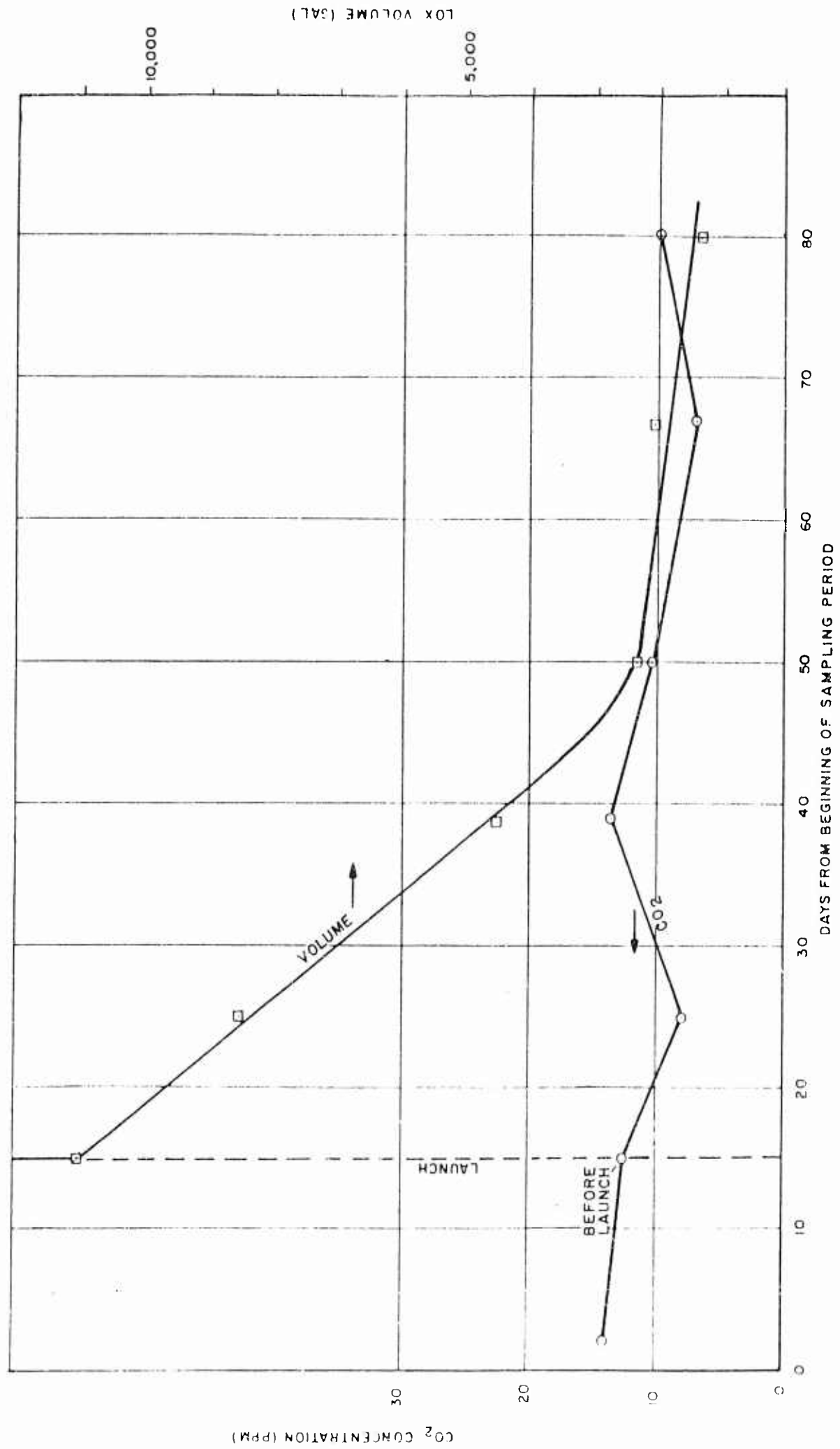


FIGURE 21 CO<sub>2</sub> CONCENTRATION PAD 12

increase of the methane concentration from the production plant to the final use of the LOX in a missile. The average concentration of methane was 13.5 ppm from the plant and 17.1 ppm from the active pads.

However, this was not the case for the inactive storage tank at Pad 12, as shown in Figure 22. In this figure, the hydrocarbon concentration and the residual liquid oxygen volume are plotted as a function of time. The last five samples were taken while the LOX was boiling off undisturbed. During this period, the volume of LOX decreased by a factor of eight, while the concentration of hydrocarbon (methane) increased only by a factor of three. Although a simple extrapolation of the hydrocarbon curve would lead one to expect that the methane concentration would not reach dangerous levels by the time all of the LOX was evaporated, the upward break toward the end of the curve shows that the methane rate of concentration may increase rapidly toward the end of the evaporation period. This would mean that the last few gallons of LOX to boil away could contain dangerous concentrations of methane.

With the exception of acetylene, no evidence was found of any hydrocarbons heavier than methane in the samples. It is not likely that any of the heavier hydrocarbons such as lubricants would be detected in the samples even if they were present in the LOX since the solubilities of these hydrocarbons in liquid oxygen are so slight as to be undetectable by the analytical techniques used. There is no simple technique currently available for monitoring insoluble hydrocarbons in liquid oxygen.

### Purity

There was no conclusive pattern to the results obtained from the purity analyses of the samples as shown in Table XII. All samples from the LOX production unit proved better than specifications (99.5%). In comparison, half of the samples from the complexes were below specifications for purity. It is reasonable to assume that the impurity was principally nitrogen and that it resulted from the technique of pressurizing the LOX tanks with nitrogen gas. It is interesting to note that Pad 14 was consistently above specifications, while Pad 20 was consistently below specifications.

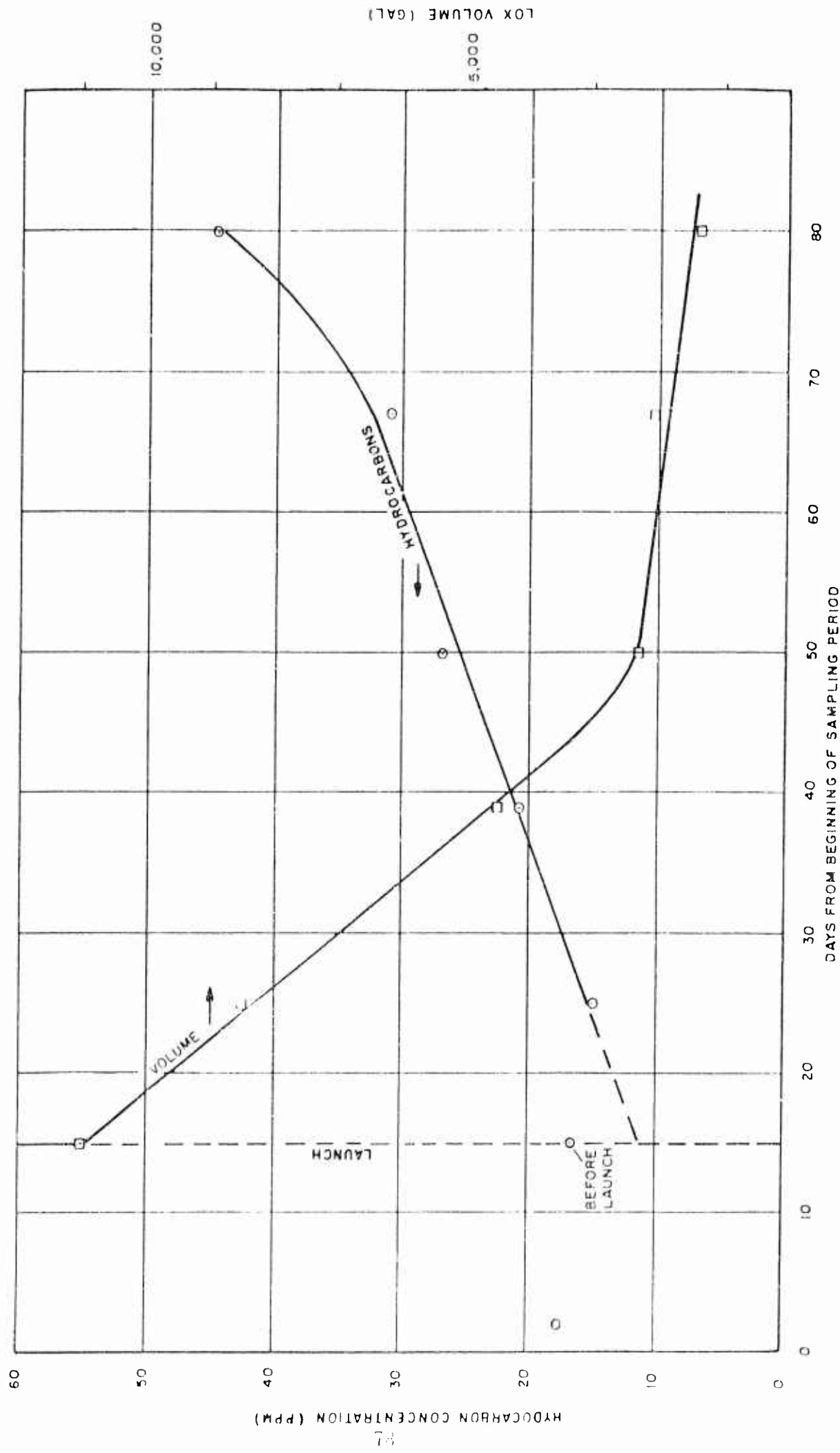


FIGURE 22 HYDROCARBONS & VOLUME PAD 12

Figure 23 shows the pattern of oxygen purity in the tank at Pad 12 as the LOX slowly boiled away. It is probable that the residual oxygen purity in the tank shortly after launch was below specifications due to nitrogen pressurization; this was followed by preferential nitrogen evaporation during the long boil-off period.

#### Effect of Activities - Storage Tanks

Relatively few samples were obtained following activities which involved the storage tanks. Examination of the results (Table X) shows little difference between these samples and the normal run of samples. However, a slight statistical trend shows that the LOX in a storage tank will be at its highest purity shortly after topping the tank.

#### Comparison of Analytical Results

Table XI presents direct comparisons between the results obtained at Air Products and the results obtained with duplicate samples at Patrick AFB Laboratory. The last sample (API No. 59) is the single sample which was analyzed by both laboratories. In general, the results between the two laboratories disagreed considerably in the analyses of CO<sub>2</sub> and methane. However, there was fairly good agreement between the purity analyses of the two laboratories.

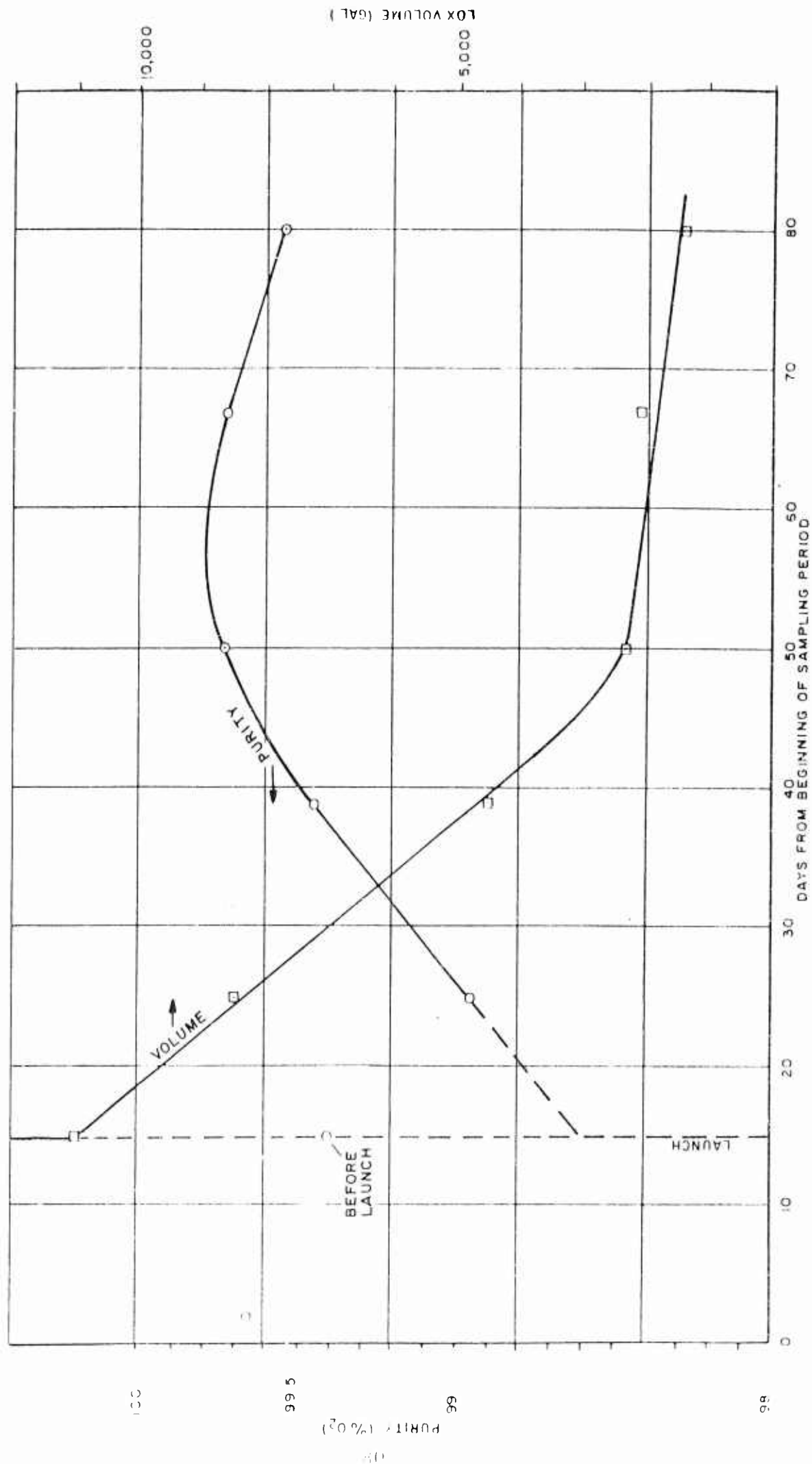


FIGURE 23 PURITY & VOLUME PAD 12

TABLE X

## SAMPLES ASSOCIATED WITH STORAGE TANK ACTIVITIES

Location (Pad)	Date Sampled	Activity	Sample Time *	Analysis		
				CO <sub>2</sub> (ppm)	Methane (ppm)	Purity (Mol %)
11	3/6	Tanking Test	1	25	22	99.55
11	3/13	Topping	1	11	15	99.45
11	3/15	Topping	14	9.5	16	99.53
13	1/16	Topping	5	13	17	99.30
13	3/15	Topping	1	25	23	99.77
13	3/20	Topping	5	13	15	99.75
14	2/1	Topping	1	14	21	99.55
14	2/17	Topping	2	14.5	15	99.65
19	1/18	Topping	1	17.5	20	99.45
19	1/25	Topping	3	15.5	13	99.40

\* Hours after activity.

TABLE XI

## COMPARISON OF DUPLICATE SAMPLES

API\* and PAFB\*\*

Location (Pad)	Date Sampled	Sample No.		CO <sub>2</sub> (ppm)		Methane (ppm)		Purity (Mol %)	
		API	PAA***	API	PAFB	API	PAFB	API	PAFB
14	2/1	16	294	14	16	21	21	99.55	99.60
20	2/2	17	307	10.5	11	13	9	99.5	99.55
14	2/9	21	365	22	1.5	20	7	99.55	99.3
14	2/17	30	496	15	4	15	4	99.65	99.65
13	3/8	43	650	17	6	15.5	4.5	99.5	99.4
11	3/13	48	691	11	0	15	4	99.45	99.6
11	3/15	51	726	9.5	5	16	7	99.53	99.4
13	3/15	53	734	25	12	22.5	0	99.77	99.7
11	3/20	57	775	10	4	16	4	99.35	99.4
13	3/20	58	778	13	11	14.5	4	99.75	99.75
11	3/16	59	743	15	5	19	3	99.45	99.5

\* Air Products, Incorporated

\*\* Patrick Air Force Base

\*\*\* Pan American Airways

### III. SUMMARY

#### SIGNIFICANCE OF CONTAMINANTS

The three significant types of contaminants in liquid oxygen are: (1) combustibles, (2) inert solids, and (3) dissolved inerts. The combustibles may range from completely soluble to completely insoluble. The chief objection to combustibles is the fire and explosion hazard should combustibles concentrate in the oxygen handling system and should an ignition source (initiator) be present. Dissolved combustibles whose lower flammability limit is greater than its solubility in liquid oxygen are not especially hazardous if the concentration of the contaminant is less than the solubility concentration. All combustibles are especially hazardous if present in concentrations greater than the solubility limit because the lower flammability concept does not apply to discrete liquid oxygen - solid combustible phases. Acetylene is the most hazardous combustible contaminant because: (1) it has very low solubility, (2) it may be present in concentrations greater than the solubility limit, and (3) it can be readily triggered into ignition.

Inert solids are hazards because they (1) may interfere with the operation of mechanical equipment, (2) may cause erosion and plugging of fluid passages, and (3) may accumulate high voltage charges of static electricity.

Dissolved inerts are principally nitrogen and argon whose presence dilutes the oxygen and adds unusable weight to the propellant system.

#### SOURCES OF CONTAMINATION

The primary source of contamination is the air stream to the separation plant which produces the liquid oxygen. Within the plant, contamination may be added by the compressors, filters and other equipment, and some contaminants are removed. The produced oxygen contains nitrogen, argon, and small amounts of acetylene, carbon dioxide, water, and light hydrocarbons.

The transfer of liquid oxygen from the plant to launch pad storage presents an opportunity for dirt, hydrocarbons, and atmospheric contaminants to

be carried into the system.

The pressurization of the stored liquid with nitrogen gas results in the accumulation of nitrogen in the liquid oxygen, as well as the introduction of contaminants which may be present in the nitrogen.

Other sources of contamination are the solvents and solids remaining from fabrication or cleaning operations, and the material contributed through deterioration of mechanical equipment.

#### DEGREE OF CONTAMINATION

Throughout the "life" of the liquid oxygen, contaminants may increase or decrease in concentration due to evaporation of a portion of the oxygen and due to inadequate mixing or "pocketing" of solids. The history of the oxygen is therefore important and should be reflected in liquid specifications and equipment design.

#### CURRENT SPECIFICATIONS FOR LIQUID OXYGEN AND EQUIPMENT

The current liquid oxygen specifications reflect confusion in the units used to express concentration. The total hydrocarbons, expressed as 22.7 ppm by weight as carbon in the use specification, is in hazardous quantities at this concentration when expressed in ppm by mole as carbon.

A comparison of the equipment cleanliness specification with the interim procurement specification shows that the liquid oxygen must contain less solids than the propellant loading system.

From this summary of the work to date on this study of liquid oxygen contamination it is apparent that consideration should be given to revising segments of the specifications, and to continue studying other segments of the specifications.

#### SOURCES AND MECHANISMS FOR IGNITION

An analysis was made of the available information on electrostatic charge generation and build up while transferring liquid oxygen. Pure liquid oxygen does not generate a charge. Charge build up is greatly enhanced

by contamination by solid particles and soluble polar materials, particularly water. The charge generation rate increases with velocity and with decrease in line diameter.

The electricity conductivity of LOX has a marked effect on charge build up. Below  $10^{-15}$  mho/cm no charge will be built up. Above  $10^{-11}$  mho/cm leakage to the ground will prevent charge build up. Monitoring the electrical conductivity of LOX and deliberate addition of non-hazardous impurity to increase the conductivity above  $10^{-11}$  mho/cm may be two new safety measures for such systems.

In general, grounding tanks and lines, maintaining a very low level of impurities and solids in LOX, and using low velocities and large diameters of flow lines are recommended.

#### CARBON DIOXIDE FILTRATION

Solid carbon dioxide cannot be satisfactorily filtered. Under the conditions occurring in the transfer of liquid oxygen at missile launching sites. The extreme turbulence existing in the warm lines and warm missile tank precludes the agglomeration of the CO<sub>2</sub> particles necessary to promote filtering.

Complete removal of both solid and dissolved CO<sub>2</sub> from the liquid oxygen is indicated, since vaporization of the liquid will cause the CO<sub>2</sub> which will not vaporize at that temperature to precipitate from solution.

However, such a recommendation cannot be made until an agreement is reached as to whether or not solid CO<sub>2</sub> in the missile liquid oxygen is a definite problem.

#### PURITY ANALYSIS SURVEY AT CAPE CANAVERAL

Liquid oxygen, as produced in the liquid oxygen facility at Cape Canaveral, meets the specifications for purity, total hydrocarbons, moisture, and acetylene as required by procurement specification MIL-P-25508C (7 November 1960).

The liquid oxygen (LOX) sampled at the various pad storage tanks at Cape Canaveral meets the specifications for total hydrocarbons, moisture, and

acetylene, but in a number of cases the LOX did not meet the specification for purity. The low purities may have been due to the technique of pressurizing LOX storage tanks with nitrogen gas.

The total hydrocarbon contamination found in the liquid oxygen was methane.

In all of the samples taken, carbon dioxide was found in quantities well above its solubility in LOX which indicates that solid CO<sub>2</sub> was present in the LOX. No conclusions can be drawn at this time as to the effects of solid CO<sub>2</sub> in liquid oxygen.

On the first samples tested, different analytical techniques were found to give different results for CO<sub>2</sub>. These differences were resolved by improving the methods used for standardizing and calibrating the infrared analyzer.

Some disagreement was found between the results as obtained by the Air Products Laboratory and those as obtained by the Patrick AFB Laboratory on equivalent samples. The disagreements have not been resolved at present but may be due to the standardizing technique used by the Patrick Laboratory for their infrared spectrophotometer.

#### IV. RECOMMENDATIONS

Based on the foregoing discussions, liquid oxygen as produced in present-day plants, both commercial and government, meets the purity and contaminant limitation requirements established for its purchase and use in the missile program. Continuous analyses are required at the production facilities and at various stages of liquid-oxygen storage and transfer to assure that these purity levels are maintained.

It is therefore recommended:

- (1) Purity analyses should be performed continuously at the generating plant on the liquid oxygen from the bottom of the low pressure column (reboiler or condenser) using a continuous monitoring thermal conductivity or paramagnetic analyzer. This instrument should have a full scale range no greater than 5.0 mol % oxygen (95% - 100% full scale range). It would be preferred, particularly if the analysis is performed by thermal conductivity that the full scale range be 1.0 or 2.0 mol % (99 - 100% and 98 - 100 purity respectively). The liquid sample should be vaporized to a gas for these analyses either by the line tap-coil vaporization technique or through the use of a separator-vaporizer device. Since warm boiling contaminants will also be determined on this sample, the separator-vaporizer device would be preferred, since it could then supply samples for all of the analysis requirements. A chemical orsat apparatus should be employed at the plant site for the analysis of calibrating and "zero" gases for use on the continuous monitoring purity analyzer. The burette should be calibrated in 0.05 ml divisions between the 99 and 100 ml marks. It should be calibrated in 0.1 ml divisions between the 95 and 99 ml marks.
- (2) Total hydrocarbon and carbon dioxide analyses should also be performed continuously on the product from the plant as removed from the bottom of the low pressure column, reboiler, or condenser. The liquid sample should be vaporized through the use of a separator-vaporizer technique wherein it is assured that no

concentration of these warm boiling contaminants can take place due to preliminary partial vaporization or fractionation. These analyses should be accomplished with a Luft principle (non-dispersive) infrared analyzer sensitized for carbon dioxide in conjunction with a catalyst furnace for the conversion of the soluble hydrocarbons to carbon dioxide. The analyzer should be of sufficient sensitivity so that the full scale range is at least as low as 0-50 ppm, and have an accuracy  $\pm 2\%$  of the full scale range. Zero and calibration gases necessary for non-dispersive infrared analysis should be checked for accuracy. Zero gas (nil CO<sub>2</sub> content) can be verified by the analyzer. Span or calibration gas can be verified by comparing it with a known CO<sub>2</sub> content gas such as air.

- (3) Acetylene concentration in the product oxygen, as removed from the bottom of the low pressure column, reboiler, or condenser, should be determined once or twice each eight hours of plant operation.

A sample should be collected as a liquid in a dewar observing the precautions concerning air contamination and precooling as outlined in the comments on sampling method A. Analysis should be by either the long or short Ilosvay (copper acetylide) method. In either case the test should be commenced on the liquid sample as quickly as possible after it has been collected to prevent excessive concentration of the acetylene due to vaporization of the sample.

- (4) Water analyses are not required on the product from a liquid oxygen plant. The equilibrium concentration of water (ice) dissolved in liquid oxygen is so low that it cannot be detected by either electrolytic hygrometry or a mirrored surface dew point apparatus. Either of these analytical techniques are capable of detecting water vapor to a level of 1 ppm (approximately -100° F dew point). An apparatus of either type is required for the stored liquid contaminant analysis described in paragraph (5) below. Occasional samples from the bottom of the low pressure column, reboiler, or condenser as obtained with the

separator-vaporizer device should be used to "zero" the water vapor analyzer. Any measurable water content in gaseous oxygen which has been derived by vaporization of liquid oxygen indicates contamination during handling operations, the water having entered the system subsequent to the oxygen generation.

- (5) Analyses of the stored liquid from the plant storage facilities and any other subsequent storage areas should be performed in a periodic manner to determine contaminant concentration due to vaporization, and loss of purity due to contamination in transfer and handling. The frequency of this testing should be dependent on the speed of movement of liquid through the storage facilities and on the opportunity for acquiring representative samples. As has been mentioned throughout the foregoing report in discussing sampling, a representative liquid sample can only be obtained from a storage tank when the liquid within the tank is well mixed immediately after some exercise has been performed on the liquid such as filling, draining, pumping, etc. The sample should be obtained by a trapped liquid vaporization technique which does not permit atmospheric contamination and which prevents the higher boiling contaminants in the liquid from concentrating due to vaporization. With a vapor sample obtained in this way, analyses for total hydrocarbon, carbon dioxide, water vapor, and purity could all be performed with the same equipment which is used for monitoring the generating plant product stream. The analysis for purity would give good insight into whether or not handling and transfer contamination had occurred before, during, or after storage. The analysis for carbon dioxide and water would also supply information concerning handling contamination problems and would give data concerning the amount of boil-off (vaporization) concentration of contaminants which occurs as the product is handled. The total hydrocarbon analysis would also give good insight into the boil-off vaporization contaminant concentration problem and would be useful in determining hazardous conditions which might exist due to hydrocarbon concentration.

The remaining analyses required on the stored liquid would be for particulate count and acetylene determination. These analyses

should also be performed periodically on the liquid in a well mixed storage facility. The most reproducible particulate matter data would be obtained by using the gravimetric technique wherein the particles contained in a certain volume of liquid are weighed after being filtered and are reported as a weight of particulate matter per standard volume. This test could easily be performed at the plant generating site where the other analytical equipment is located. It would require a filtering device, a specialized analytical balance, oven, and relatively small amounts of reagents and laboratory glassware. The acetylene determination could be performed at the sample site with the portable quick test apparatus and if any indication of acetylene is evident, a sample should be returned as quickly as possible to the laboratory facility at the generating plant where equipment for performing the long test might be located.

With the above scheme of continuous and intermittent analyses, a complete knowledge of the purity and the major contaminants will always be available for the user. Plant product will be continuously analyzed so that an average purity and contaminant level will be available for investigation and the major problems concerning safe operation of the plant will be overcome. Depending on the frequency of the intermittent analyses from the storage facilities, any increase in contaminant level or decrease in purity due to mishandling or excessive vaporization in the storage tank could be ascertained and remedied.

#### SPECIFICATIONS

##### Maximum Limits

Total Hydrocarbons	500 ppm (methane equivalent - mole basis)
Acetylene	4 ppm (mole basis)

These maximum limits provide little margin for safety and must be regarded as unsafe. It is recommended that, if total hydrocarbons reach 500 ppm or acetylene reaches 4 ppm, no further handling be performed except for immediate emergency measures designed to safely dispose of the liquid oxygen.

The maximum limit for acetylene is based on the solubility of acetylene in liquid oxygen. Hydrocarbons containing more than four carbon atoms would not appear in detectable amounts in the course of routine operations, so the maximum limit of 500 ppm for total hydrocarbons is based on the solubility limit of isobutylene, the least soluble of the light hydrocarbons. Isobutylene is rarely found in liquid oxygen, and it is considered that the maximum limit of 500 ppm, which is also taken as the basis for use and procurement limits, is conservative for the normal run of liquid oxygen. Methane generally comprises the bulk of the total hydrocarbons in liquid oxygen and the maximum limit could be relaxed considerably if methane concentration were determined separately.

#### Use Limits

Total Hydrocarbons	315 ppm (methane equivalent - mole basis)
Acetylene	1.2 ppm (mole basis)
Particulate Matter	2.9 mg/liter

The use limits are considered to apply at the last point that corrective action can be taken, that is, in the storage tank used to supply the missile tank. At times, it is necessary to load liquid oxygen into a missile tank, hold for a period of time and subsequently return the liquid oxygen to the storage tank. The use limits recommended for total hydrocarbons and acetylene are based on the supposition that liquid oxygen will pass twice through a load-unload cycle and that the resulting concentration should not exceed 90% of the maximum limit. If experience with a particular load-unload system shows that a different vaporization rate occurs, the use limits should be revised accordingly.

The suggested use limit of 2.9 mg/liter for particulate matter is based on a tank-cleaning specification which allows this amount of contamination. It is of little value to require that liquid oxygen in a tank be cleaner than the tank-cleanliness permits.

No use limit is suggested for argon since it is presumed that, due to preferential vaporization, argon concentration will always be lower than procurement specifications.

No use limit is suggested for nitrogen because nitrogen pressurization may

or may not be used. The limit for nitrogen impurity must be determined for individual facilities and will depend on the mission requirements.

No use limit is suggested for carbon dioxide and water because the effect of solids on the intended use of the liquid oxygen, an important part of this program, has not yet been studied

#### Procurement Specifications Limits

Total Hydrocarbons	50 ppm (methane equivalent - mole basis)
Acetylene	0.2 ppm (mole basis)
Total Impurities	0.5% (mole basis)

The procurement specifications are considered to apply to the point at which liquid oxygen enters the propellant-loading system, i.e., the trailer delivering the liquid oxygen from the plant to the launchsite storage. With this specification, proper quality control can be exercised by producers who may be supplying liquid oxygen from a number of different generating sites.

The above procurement specifications are based on the established ability of liquid oxygen manufacturers to supply liquid oxygen of the required quality on a routine basis. Under normal handling conditions, liquid oxygen may undergo a total vaporization of 75 percent from the time of procurement to the time of final use in a missile. This figure has been estimated from the following assumptions: 13 percent is lost while loading a trailer from a tank car and unloading into the launchsite storage tank; 0.25 percent per day is lost from the storage tank; the liquid oxygen is stored for one year; two cycles of loading and unloading the missile tank are performed with 15 percent loss in each cycle. Thus, it can be seen that the non-volatile impurities may be concentrated about fourfold from procurement to use. Starting with the procurement specifications, the total hydrocarbon content at use would be 200 ppm and the acetylene content would be 0.8 ppm, well below the respective use limits of 315 ppm and 1.2 ppm.

The total impurities are principally argon with small amounts of nitrogen, acetylene, hydrocarbons, carbon dioxide, and water. With

a 75 percent vaporization loss, the original total impurities will have dropped from 0.5% to about 0.3%.

## OPERATION

### Equipment Design

#### Launch-Site Repurification

In present liquid-oxygen propellant-loading systems, the ever-changing composition of the liquid, due to evaporation, will result in the accumulation of contaminants to a point which may threaten safety and reliability. At the present time, the only means for dealing with this condition is to periodically discard some of the liquid oxygen. Discarding liquid oxygen may also be necessary in the event of unexpected contamination. Both conditions could be remedied by use of launch-site repurification, with possible economic or tactical advantages over the periodic dumping of liquid oxygen.

Based on current industrial practice in liquid-oxygen generators, purification by adsorption is the recommended approach. Using this technique, liquid oxygen from a launch-site storage tank would be recirculated through an external adsorber for removal of the contaminants. The effectiveness of this system would depend upon the adsorber design and storage tank configuration. An expanded discussion of adsorber design and repurification rates is presented in Appendix B.

It is recommended that a detailed study be made of the possibilities of repurification by adsorption. This study would require additional design analysis and experimental work. It is expected that the economics of repurification would be reasonable in view of the increased reliability of the launch-site equipment.

#### Improvement of Equipment and Piping

As indicated under "Degree of Contamination", present equipment and piping, in some cases, leaves much to be desired. It is recommended that present equipment and piping be examined with a view toward eliminating dead ends and providing adequate through flow. To accomplish

this, it may be necessary to rearrange piping or install drain lines. Some specific examples are rearrangement of the piping on storage tanks as indicated in Figure 3, and installation of a drain line on liquid-oxygen catch-tanks (Figure 4).

It is further recommended that consideration be given to positive flushing action in the design of future installations. For example, storage tanks could be designed for vertical orientation, with conical bottom sections as illustrated in Figure 24.

#### Transfer Procedure

It has been stated in the Discussion, that one of the major sources of atmospheric contamination is the transfer operation in which temporary connections are frequently made and broken. It was also pointed out that contamination can occur either by trapping a portion of the atmosphere in a warm line or by allowing the atmosphere to enter and deposit condensables inside cold equipment. Both mechanisms for contamination can be controlled by strict adherence to proper procedures. The trapped portion of the atmosphere may be removed by adequate purging before transferring, and condensables may be prevented from entering cold equipment by allowing the equipment to warm before disconnecting.

It is recommended that suitable transfer procedures be established and followed in order to reduce atmospheric contamination. In some cases, it may be necessary to redesign transfer piping in a manner similar to the arrangement shown in Figure 25. With such an arrangement, suitable performance could be obtained using a procedure such as follows:

Using normal practice in removing caps and seals prior to making such connection, the supply unit and liquid receiver are connected with flexible hose.

Valve No. 1 of the supply unit is opened and the initial vapors, followed by liquid, are allowed to flow through the hose and vent through Valve No. 2.

When liquid oxygen discharges through the vent from Valve No. 2, valves No. 3 and No. 4, which are normally closed, are opened; Valve No. 2 is then closed, diverting flow through the filter to

the vent through Vent No. 4.

When liquid flow reaches the discharge of the vent line through Valve No. 4, Valve No. 5 is opened and Valve No. 4 is closed.

Transfer proceeds between the supply unit and the receiver

When transfer is complete, Valves No. 5 and No. 1 are closed, and Valve No. 4 is immediately opened to vent, followed by closing Valve No. 3 and opening Valve No. 2.

When gas flow through Valve No. 4 vent is reduced, Valve No. 4 is closed; the filter is isolated and as it continues to warm, the filter pressure will increase until the pressure relief valve opens (at a nominal pressure of 100 psig).

When the flexible hose temperature exceeds the dew point of the ambient air (as indicated by the disappearance of frost), uncoupling may proceed, using normal practice in replacing caps and seals as soon as each disconnect is made. If defrost of the line is too prolonged for the operations concerned, flowing water or other means of increasing the heat flow to the line may be employed.

The above arrangement and procedure would be a valuable step in a program aimed at controlling unpredictable contamination, and could be provided at small capital expense.

It is further recommended that consideration also be given to other approaches such as dry nitrogen blanketing and quick-disconnect fittings.

Further work should be done on the problem of solid CO<sub>2</sub> in missile liquid oxygen. Tests should be conducted to determine if that material does actually create undesirable conditions during a missile tanking or shoot. If the answer is positive, the CO<sub>2</sub> should be removed by filtration and adsorption; if negative, a filter assembly should be designed which will pass the CO<sub>2</sub> particles but withhold other undesired particles (rust, sand, lint, etc.)

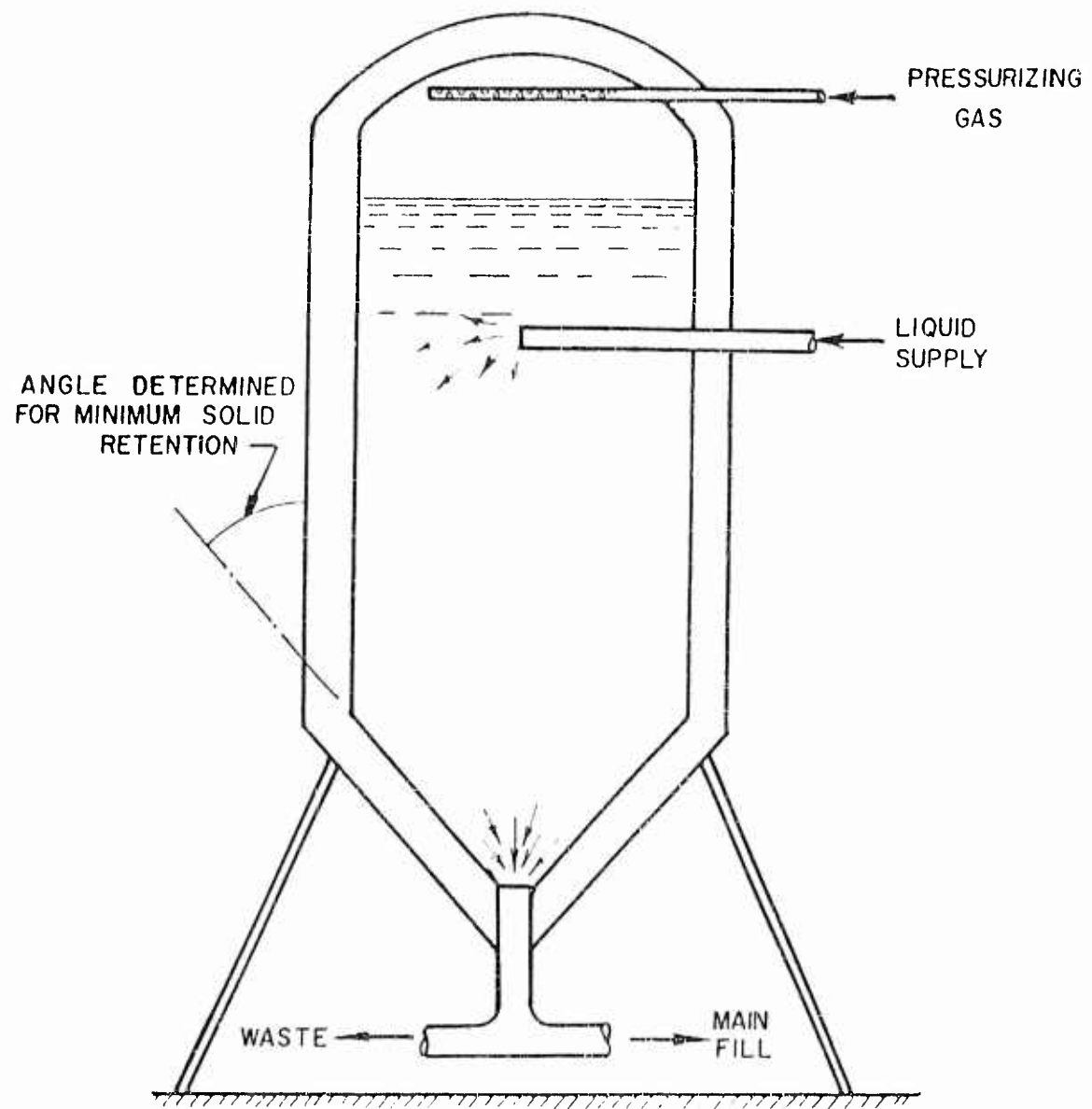


Figure 24 - A PROPOSED LIQUID OXYGEN STORAGE TANK  
ARRANGEMENT FOR MAXIMUM FLUSHING ACTION BY THROUGH-FLOW

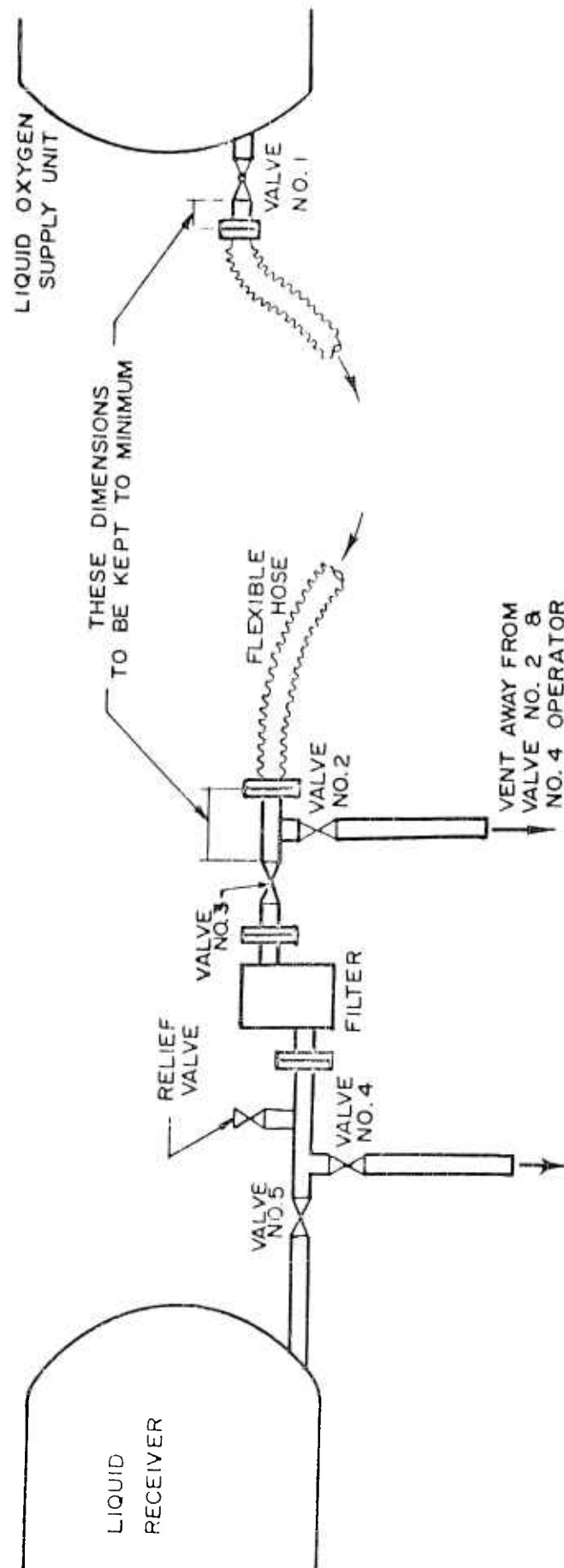


Figure 25 - AN ARRANGEMENT FOR TRANSFER CONNECTIONS TO MINIMIZE  
CONTAMINANT INTRODUCTION

### Film Ignition

It is strongly recommended that further work be done on the ignition of hydrocarbon films. If the proposed 100 milligram per square foot limit can be substantiated by further tests with other greases, oils, etc., the missiles program may save much money, time and in some cases, project delays by the simplification of present cleaning methods.

Static Charge Generation: does not seem to be a problem in handling of liquid oxygen having the normal amounts of contamination. The normal procedures of grounding equipment, preventing sloshing in tanks, etc. should be followed.

### Purity Analysis Survey at Cape Canaveral

With the exception of the possible additional carbon dioxide requirement as outlined below, the Air Force should maintain MIL-P-25508C (Military Specification, Propellant, Oxygen) as it exists regarding the level of purity, and the amounts and types of impurities present in liquid oxygen.

It should be determined if the presence of solid carbon dioxide in a missile tank is detrimental to the operation of its liquid oxygen flow and flow control system.

Until such time as it is determined whether CO<sub>2</sub> is a hazard in a missile system, the procurement specification should be revised to limit the level of carbon dioxide to below its solubility in liquid oxygen. This value is approximately 5 ppm (molar) at the normal boiling point of liquid oxygen.

It is suggested that the Patrick Laboratory incorporate a calibration gas preparation procedure similar to that used at the Edwards Air Force Base Flight Test Center Laboratory. This apparatus utilizes a micro-manometer to measure the volumes of gas used in preparing the standardization mixtures, and the mixtures are prepared directly in the analyzer gas cell, eliminating potential errors from gas transfer or diffusion. (This standardization technique was used at Edwards Air Force Base in preparing a methane in oxygen calibration curve. The results of three analyses for methane on the Edwards 75 tons per day Plant liquid oxygen product showed an average of 13.5 ppm. The results of all of the analyses for methane from the identical 75 tons per day Plants at Cape Canaveral in this report also averaged 13.5 ppm.)

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## APPENDIXES

## APPENDIX A

### LIMITS FOR FLAMMABLE CONTAMINANTS

#### 1. Flammability Limits

For a mixture to be flammable, several conditions must exist (5, 16). Proper quantities of fuel and oxidant as well as a source of ignition must be present. An exception to this rule is the decomposition under certain conditions of some chemicals which have negative heats of formation - acetylene, silver acetylide, ozone, and others - without the need of any agent. These materials are hazardous by themselves and play a part in ignition. Hazardous conditions, in general, are avoided by preventing the simultaneous appearance of all three of these factors.

In the case of liquid oxygen the oxygen, obviously, serves as the oxidizer and cannot be eliminated. Not all sources of ignition are known, so positive control of the mechanism of ignition is difficult. Control of the fuel remains as the safest means of avoiding a hazardous condition. However, the avoidance of fuels does not necessarily mean that ignition sources or initiators are to be ignored.

Much is known about flammable limits of gases in air (5), and the underlying theory of combustion has been studied extensively (16). Data on combustible limits in gaseous oxygen, although not as complete as in air, are also available. However, data on combustible limits in liquid oxygen are very meager, although this is not as great a handicap as it might seem. Further discussion will show that safe generalizations may be used as guides for combustible limits with liquid oxygen.

Table A-I presents the lower flammability limits for various gases in both air and oxygen at ambient temperature and atmospheric pressure. It can be seen that the limits for all of the gases listed are practically the same for both cases, indicating that the limits are set by the concentration of fuel, providing sufficient oxygen is

present. On this evidence, it may be presumed that flammability data obtained with air may be used as if it were obtained with gaseous oxygen. It is also interesting to note that, on a methane equivalent basis, flammability limits for the hydrocarbons are all approximately the same.

Comparing flammability limits in liquid oxygen versus flammability limits in gaseous oxygen, it may be predicted that, in general, more fuel will be needed with liquid oxygen than with warm gaseous oxygen. This prediction is supported by a consideration of the requirements of combustion. For combustion to be self-supporting, sufficient energy must be produced by the burning portion to raise the adjacent mass to kindling temperature. If liquid oxygen is used in place of gaseous oxygen, additional heat is required both to vaporize the oxygen and fuel and to warm the vapors to ambient temperature. This additional heat can only come from additional fuel. Thus, it may be assumed that, where experimental flammability data is lacking for liquid oxygen, margin of safety is supplied by using data obtained with air or gaseous oxygen.

## 2. Solubility

In the above discussion of flammability limits, it was assumed that the mixtures of fuel and oxygen were homogeneous. However, in actual circumstances it is unlikely that concentrations of hydrocarbons would be permitted to approach the flammability limit. Table A-II presents the solubilities of the various hydrocarbons in liquid oxygen compared with their lower flammability limits. Solubility as a function of temperature is presented for the saturated hydrocarbons in Figure A-1 and for the unsaturated hydrocarbons in Figure A-2. It can be seen that, except for methane, ethane, and propane, the solubility limit is reached well below the flammability limit. Concentrations above the solubility limit are as hazardous as concentrations above the flammability limit. This means that hazard tolerance should be based on solubility limits instead of flammability limits.

Although solubility is generally thought of as equilibrium between solid and liquid phases, it can also be considered to be equilibrium between immiscible liquid phases. Ethane, propane, ethylene, and propylene are all reported (6, 18, 19) to form conjugate phases with liquid

oxygen. In the cases of ethylene and propylene, the formation of a second, fuel-rich, liquid must be considered in the same category as the formation of a solid phase, and with the same degree of hazard. The concentration of hydrocarbon in the oxygen rich phase would be termed the solubility. Considerable data on solubilities of combustibles in liquid oxygen are available in the literature (6, 8, 10, 11, 13, 14, 16, 18, 19, 22, 23, 25 and 31).

### 3. Initiators

An initiator is defined as an energy source of such a magnitude and intensity that a fuel-oxidant reaction can occur providing the fuel-oxidant mixture concentration is within the flammability region. Initiators can be chemical, thermal, electrical, and mechanical in nature. The intensity of the energy source refers to the energy (or temperature) level, and magnitude refers to the total quantity of energy released as kindling. The potential chemical initiators, ozone, and the nitrogen oxides are discussed at length below. A discussion of thermal initiators such as electric matches, blasting caps, external heat, and thermite bombs is beyond the scope of this project. Electrical initiators such as static electricity discharge, which is generated within the liquid oxygen handling system, are a part of this project. Mechanical initiators such as adiabatic bubble compression, fluid friction of high velocity solid particles, mechanical friction of valves, and pump bearings and shock waves induced by 'water hammer' also will be studied.

Ozone has been shown experimentally to react with unsaturated hydrocarbons at liquid oxygen temperatures and to increase the ignition sensitivity of liquid oxygen-fuel mixtures in the flammability region (14). Flammable mixtures of liquid oxygen-fuel have been ignited by ozone (4, 14, 18, 23, 28). Explosive reactions between ozone and nitrogen trioxide or tetroxide at temperatures well above  $-297^{\circ}\text{F}$  (29) and explosive decomposition of ozone itself at  $-150^{\circ}\text{F}$  (12) have been reported. In all experimental work, relatively large quantities of ozone were used. However, despite the evidence of its ability to initiate combustion, there is no reported evidence in the literature of the presence of ozone in liquid oxygen. One team of investigators report the possibility of trace quantities (22).

Experiments with nitric oxide and nitrogen dioxide show that neither react with unsaturated hydrocarbons at  $-297^{\circ}\text{F}$  and that they do not increase the ignition sensitivity (in some cases, even lowering the sensitivity) of flammable liquid oxygen-hydrocarbon mixtures (14). If ozone (at least more than 200 ppm ozone for mixtures studied) is introduced into flammable liquid oxygen-unsaturated hydrocarbon mixtures containing nitrogen dioxide, the ignition sensitivity is increased to a greater extent than that due to ozone alone (14). Nitrogen dioxide added to a liquid oxygen-ethane mixture just below the lower-flammable-limit concentration had no effect on the limit (18). Nitric oxide reacts with oxygen at temperatures slightly above  $-297^{\circ}\text{F}$  and very violently at  $-265^{\circ}\text{F}$  (21).

Experiments with gaseous nitrous or nitric oxides have shown them to be flammable but no ignition occurred when each solid oxide was slurried in liquid oxygen (18). Cocrystals of nitrous oxide and acetylene containing more than 25 mol percent of the latter were observed experimentally to have the same ignition sensitivity in liquid oxygen as acetylene (26).

Data on the presence of initiators and sensitizers in liquid oxygen and knowledge of their effects are meager. The safest course appears to be the avoidance of flammable liquid oxygen-fuel mixtures and the prevention of the occurrence of chemical, thermal, and mechanical initiators.

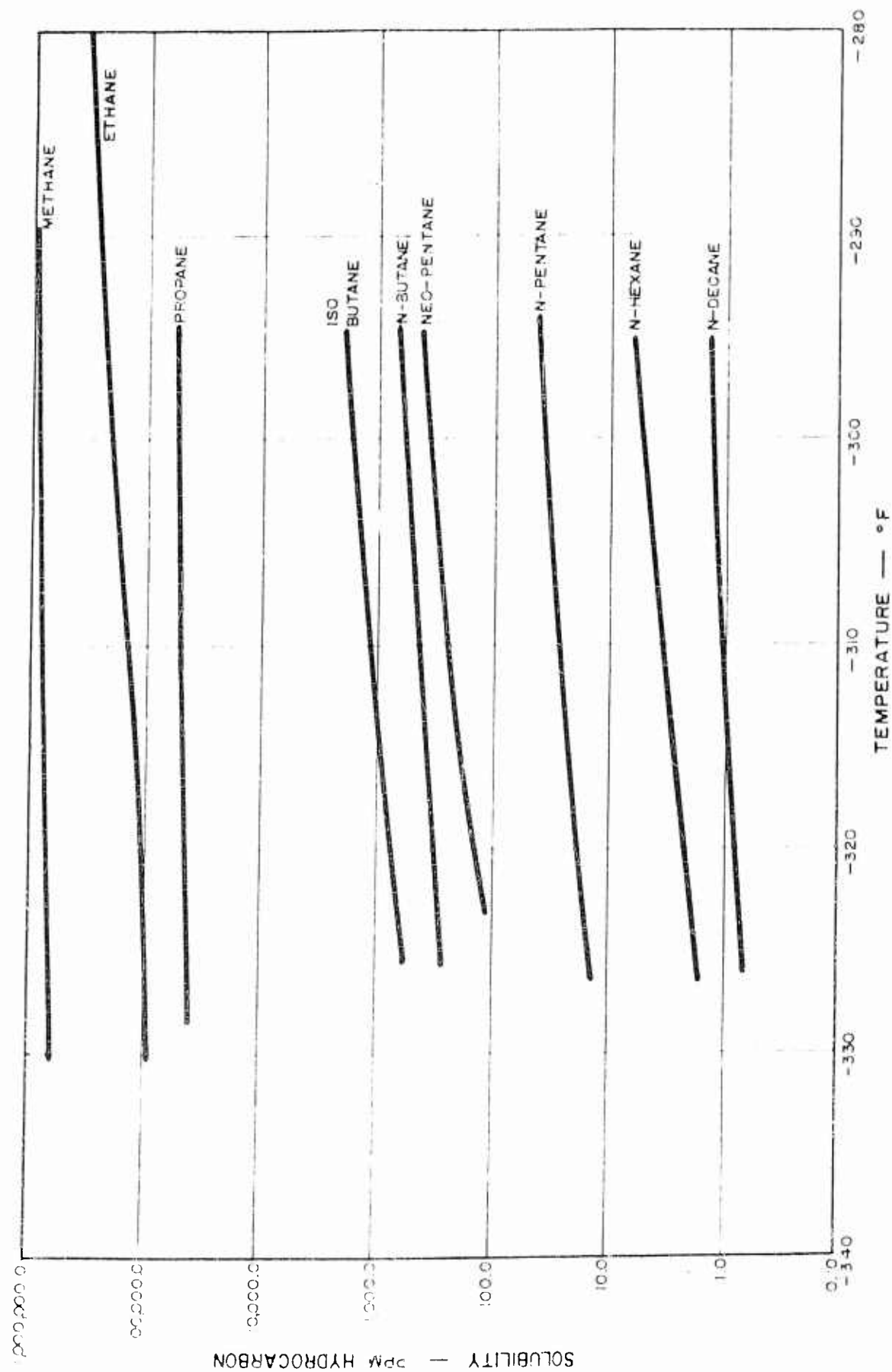


FIGURE A-1 - SOLUBILITY OF SATURATED HYDROCARBONS IN LIQUID OXYGEN (19)

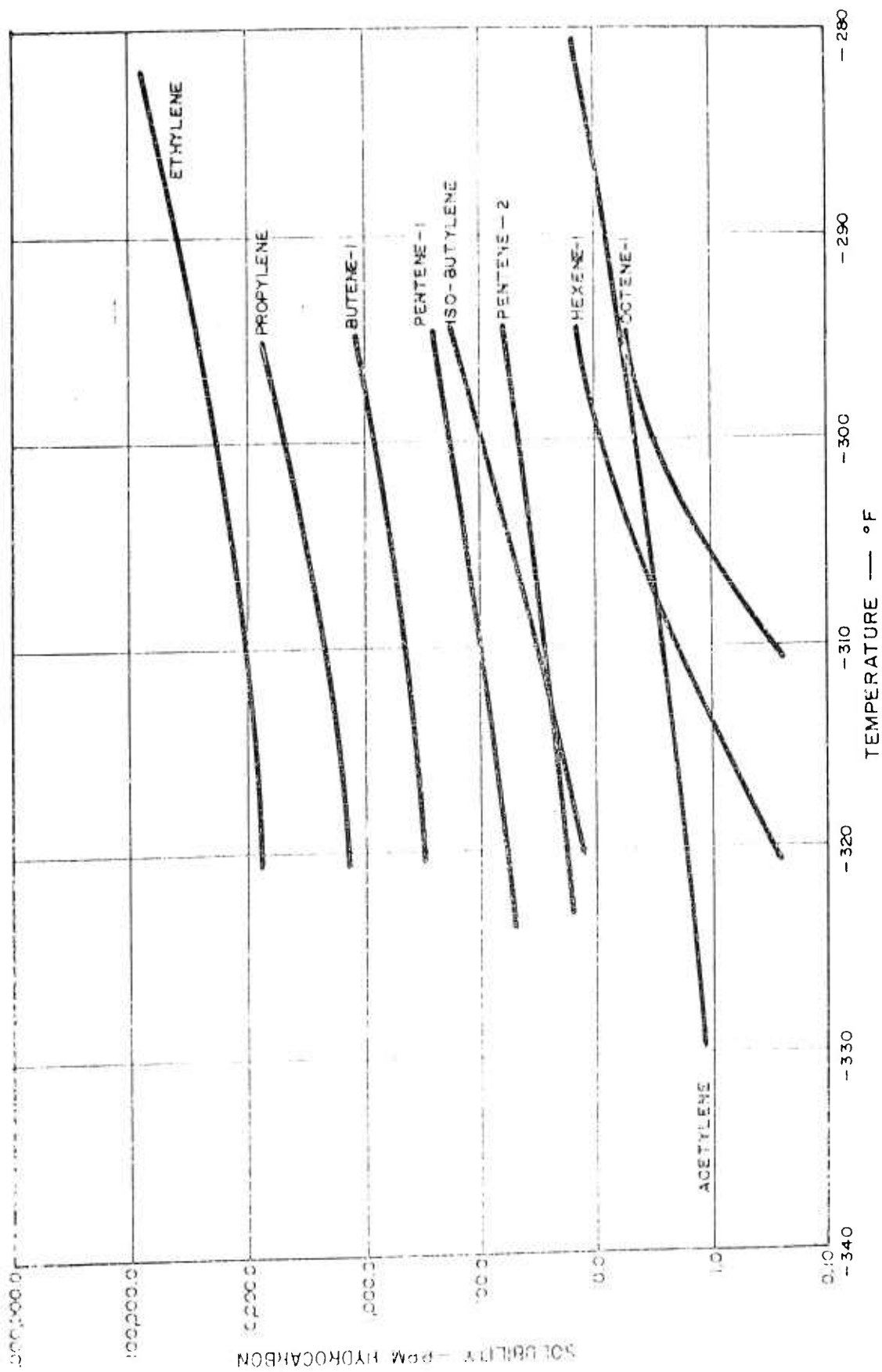


FIGURE A-2 - SOLUBILITY OF UNSATURATED HYDROCARBONS IN LIQUID OXYGEN (19)

TABLE A-I

LOWER FLAMMABILITY LIMITS OF COMBUSTIBLES

<u>Gas</u>	<u>Air*</u>	<u>Oxygen (Gas) *</u>	<u>Oxygen (Liquid)**</u>
Hydrogen	4.0	4.0	----
Methane	5.0	5.1	11.0
Ethane	3.0	3.0	4.0
Propane	2.2	2.3	----
Butane	1.9	1.8	----
iso-Butane	1.8	1.8	----
Ethylene	2.7	3.0	----
Propylene	2.0	2.1	----
Butene-1	1.6	1.8	----
Butene-2	1.8	1.7	----
i-Butylene	1.8	---	----
Carbon Monoxide	12.5	15.5	----

All values are given in mole percent (not methane equivalent).

\* Reference 5 , ambient temperature, atmospheric pressure.

\*\* Reference 18 , -297°F, atmospheric pressure.

TABLE A-II

SOLUBILITY OF HYDROCARBONS IN LIQUID OXYGEN  
Parts Per Million by Mole

<u>Gas</u>	<u>Solubility* at -297.3°F (Methane Equivalent)</u>	<u>Lower Flammability Limit (Methane Equivalent)</u>
Methane	980,000	50,000
Ethane	430,000	60,000
Propane	150,000	63,600
Ethylene	55,000	55,000
Propylene	20,100	60,000
1-Butane	7,640	72,000
Butene-1	4,000	64,000
n-Butane	3,440	74,400
1-Butylene	530	72,000
Acetylene	10	50,000

\* Reference 19

## APPENDIX B

### ADSORPTION REPURIFICATION OF LIQUID OXYGEN

Since low-temperature adsorption-purifiers are already used in air-separation plants to remove hydrocarbon contaminants and carbon dioxide, adsorptive purifiers can be designed for stored liquid oxygen based on this experience. The difference between the purification of stored liquid oxygen and purification in an air-separation plant lies in the different conditions used for the process. The hydrocarbon adsorbers in a generating plant normally operate at about  $-280^{\circ}\text{F}$  and 75 psia whereas adsorbers purifying stored liquid oxygen would operate at about  $-297^{\circ}\text{F}$  and slightly above atmospheric pressure. The effect of temperature on adsorber capacity has not been completely established, but it may be particularly important for the components with low solubilities which are of interest.

Available data show that the adsorptive capacity for contaminants decreases with a decrease in inlet concentration. Since the concentrations to be handled in launch-site storage are lower than the concentrations dealt with in air plants, the concentration difference must also be considered in adsorber design. Although conservative criteria may be used for the safe design of adsorptive repurification systems, it is desirable to obtain more quantitative data on adsorbent characteristics before establishing final designs.

Since the build-up of contamination in stored liquid oxygen is generally a gradual process, it would not be economically desirable to build individual repurification units which would be idle much of the time.

#### Repurification Rate

The purification rate of a recirculation-adsorber depend primarily upon the size of the circulation pump and the extent of mixing in the storage tanks. During repurification through an external adsorber the liquid oxygen would be subject to additional heat influx due to the adsorption operation. Liquid-nitrogen refrigeration could be used to recondense any boil-off resulting from such heating.

In the simplified analysis of repurification rates which follows, liquid-nitrogen recondensation of the boil-off oxygen is assumed. (The amount of liquid nitrogen

required would be small.) In addition, it is assumed that the circulating oxygen leaves the adsorber completely free of contamination, although it is recognized that this is true only for a perfect absorbent.

The following simplified models are considered in evaluating the probable repurification rate:

1. Complete By-Passing

If the positions of the inlet and outlet lines leading to and from the repurification system are close to each other in the storage tank, it is possible that complete by-passing will occur. Liquid oxygen flowing to the adsorber will have been already purified and essentially no purification will take place after an initial active volume has been circulated through the purifier. The positions of the inlet and outlet lines in the storage tank, therefore, must be arranged to promote thorough mixing of the contents. (Refer to Figure 3 in the body of the report.

2. Complete Mixing

For the case of complete mixing, the concentration of contaminant will decrease according to the equation:

$$-\frac{dC}{dt} = kC$$

where

C = concentration of contaminant in liquid oxygen.

t = time after start of purification, hours.

k = purification coefficient (capacity of pump per hour divided by storage tank capacity).

The integrated form of this equation yields the new concentration, C, of the impurity in question:

$$\ln \frac{C_0}{C} = kt$$

where

$C_0$  = initial concentration of contaminant.

The "half-life" of the purification system, i. e., the time required to reduce the contaminant concentration by a factor of two is:

$$t_{1/2} = \frac{0.694}{k}$$

Thus a tank containing 24,000 gallons and connected to an external repurifier circulating liquid oxygen at a rate of 100 gpm will have a "half-life" of:

$$t_{1/2} = 2.78 \text{ hours}$$

### 3. Plug Flow

In the case of plug flow, the time to remove all the contaminant is proportional to the volume of liquid in the vessel divided by the pump rate. For a 24,000 gallon tank and 100 gpm pump, the liquid will be completely purified in 240 minutes, or 4 hours. This, of course, is for ideal conditions and will not happen except when pumping the entire contents from one tank to another. Interestingly, the "half-life" for plug flow is not much less than that for complete mixing, i. e., concentration decreases linearly with time:

$$t_{1/2} = \frac{0.5}{k}$$

For the example cited, the "half-life" would be 2.00 hours as compared to 2.78 hours for complete mixing.

### 4. Actual Flow

Actual recirculation flow will be a mixture of the three possible flow conditions with the decrease in contaminant concentration being somewhere between the rates for the two extreme cases of flow, i. e., plug flow and complete by-passing. In launch-site storage tanks equipped with inlet and outlet piping arrangements such as illustrated previously in Figure 3(b), the flow pattern should be more favorable to rapid repurification; the rate of decrease in contaminant concentration could be expected to be closer to that for plug flow and complete mixing than for complete by-passing.

APPENDIX C

LIST OF FILTER VENDORS

Aircraft Porous Media, Incorporated  
Glen Cove, New York

Arno Engineering Corporation  
Meriden, Connecticut

Bendix Filter Division, Bendix Aviation Corporation  
Madison Heights, Michigan

Carborundum Company  
Perth Amboy, New Jersey

Commercial Filters Corporation  
Melrose, Massachusetts

Dollinger Corporation  
Rochester, New York

Harmon Equipment Company  
Los Angeles, California

Micro Metallic Division, Pall Corporation  
Glen Cove, New York

Puroator Products, Incorporated  
Rahway, New Jersey

## APPENDIX D

### STATIC ELECTRICAL DISCHARGE IN LIQUID OXYGEN SYSTEMS

#### INTRODUCTION

Electrostatic charge accumulation and discharge are some of the more common hazards in handling flowing liquid oxygen. Normal safety practice is to ground tanks, transfer lines, and handling equipment. A better understanding of the mechanism of electrostatic charge build up will contribute to safer transfer of liquid oxygen.

#### NATURE OF STATIC CHARGE

When the surfaces of two poor conductors of electricity are brought together and separated, electrons, and sometimes ions, cross from one surface to the other, resulting in equal and opposite charges on the two surfaces. The two surfaces can be continuous or non-continuous, both moving, or only one moving (e.g.: A fluid moving through a pipe, two phase flow in a pipe, solid particles settling in a fluid).

The limits of the amount of charge that can be accumulated are due to the electrical conductivity of the system; i.e. to the rate of leakage of the charge from the system.

The factors affecting charge accumulation and ignition hazard are:

- a. Geometry of the system.
- b. Flow characteristics.
- c. Electrical properties of fluids and systems.
- d. Nature and amounts of impurities.

#### BASIC CONCEPTS

The basic concepts of static electricity generation and build up have been reviewed by Klinkenberg (15) and Loeb (17). The engineering applications of Klinkenberg's study to other systems have been reviewed by Saletan (27). The concepts and applications that will be used in this report are summarized

below:

1. Rate of charge generation as a function of flow characteristics

$$i_s = 1/2 f HRe \epsilon E E_0 U Z$$

where  $i_s$  = Streaming current = rate of flow of electrical charge into the fluid (amp).

$f$  = Fanning friction factor

$HRe$  = Fluid Reynolds number

$E$  = Dielectric constant of fluid

$E_0$  =  $8.85 \times 10^{-14}$  amp. sec/volt cm.

$U$  = Average fluid velocity (cm/s).

$Z$  = Zeta potential - the interface potential where the charges are transferred to the fluid, usually 0.01 - 1 volts.

2. Rate of charge leakage from a charged system.

$$Q = Q_0 e^{-\frac{t}{T}}$$

where  $T = \frac{EE_0}{k}$  = relaxation time (= time constant; sec.)

$Q$  = Total charge in fluid (Coul).

$Q_0$  = Total charge in fluid at some arbitrary time (Coul).

$t$  = Time for charge to drop from  $Q_0$  to  $Q$  (sec).

$k$  = Electrical conductivity of fluid (mho/cm).

3. Streaming potential. The potential between the ends of a pipe which a fluid is flowing and accumulating a charge.

$$V_s = i_s \frac{l}{A k}$$

where  $V_s$  = Streaming potential (volts).

$l$  = Length of pipe (cm).

$A$  = Cross section area of pipe (cm<sup>2</sup>).

4. Energy of discharge.

$$E = \frac{1}{2} E E_0 \frac{A}{l} V_s^2 = \frac{1}{2} \frac{E E_0 l}{A} \frac{i^2}{k^2}$$

where  $E$  = Energy of discharge (Joule).

#### IGNITION HAZARD

The minimum ignition energy for volatile organic solvents in oxygen is 0.2 m.j. (16).

Tournay et al (30) have studied the susceptibility of liquid oxygen explosives made from a solid adsorbent (90% or more activated carbon) soaked in liquid oxygen, to electrostatic discharge. The most sensitive materials required more than 2 Joules to initiate a detonation.

It can be safely assumed that at least 0.2 m.j. and probably one or two orders of magnitude above this value would be required to initiate a detonation of liquid oxygen with a combustible material.

#### EFFECT OF THE GEOMETRY OF THE TRANSFER LINE

For the same flow rate

$$Re \propto \frac{1}{D}$$

where  $D$  = diameter of the line (cm)

$\propto$  = proportionality sign.

$$\begin{aligned}
 &\text{and} & U &\propto \frac{1}{D} \\
 &\text{For laminar flow} & f &\propto \frac{1}{N_{Re}} \\
 &\text{For turbulent flow} & f &\propto (N_{Re})^{-0.2} \\
 &\text{since} & i_s &= \frac{1}{2} f N_{Re} \pi E E_0 U Z \\
 & & i_s &\propto D^{-2} = D^{-2.8} \\
 &\text{since} & E &= \frac{1}{2} \frac{E E_0 l}{A} \frac{i^2}{k^2} \\
 &\text{and} & A &= \frac{\pi}{4} D^2 \\
 & & E &\propto D^{-6} = D^{-6.8} \\
 & & E &\propto 1
 \end{aligned}$$

The energy of discharge would be decreased greatly by a slight increase in diameter of the line. It would also decrease to a smaller extent by a decrease in the length of the pipe. For very narrow lines, however, the increased rate of charge leakage due to proximity to the wall would offset the effect of decreasing diameter.

#### EFFECT OF FLOW CHARACTERISTICS

The Zeta potential (17) is a function of the thickness of the charged zone at the interface where charge separation takes place, and therefore it is a function of the velocity and flow pattern.

For the same fluid and geometry

$$V_s \propto f U^2 Z$$

The pressure drop ( $\Delta P$ ) is related to the velocity by (24) the relationship

$$\Delta P \propto f U^2$$

Bocquet et al (3) have shown that the ratio  $V_s / \Delta P$  is independent of the Reynolds number over a wide range. This indicates that the change of  $Z$  with flow conditions is small.

since for laminar flow  $f \propto U^{-1}$

and for turbulent flow  $f \propto U^{-0.2}$

$$i_s \propto U - U^{1.8}$$

For turbulent flow and kerosene the streaming current was found experimentally (15) to be proportional to  $U^{1.75}$

$$\therefore E \propto U^2 - U^{3.6}$$

Decreasing the linear velocity of LOX would therefore decrease the ignition hazard.

Two phase flow should be avoided as larger amounts of moving interphase surfaces are available for rapid charge separation.

#### EFFECT OF THE ELECTRICAL PROPERTIES OF FLUIDS AND SYSTEM

##### 1. Sign of Charge

With water and with most other impurities LOX becomes negatively charged. Since most fuels flowing through a transfer line become positively charged, this increases the ignition hazard when pumping LOX and fuel at the same time into missile tanks.

##### 2. Grounding

Grounding the lines and tanks decreases the potential between fluid and walls and enables leakage of the charge from the fluid to the ground. Grounding, however, does not eliminate the ignition hazard from the charged fluid.

##### 3. Electrical Conductivity of LOX

Pure LOX is a very poor conductor. Small amounts of polar impurities increase its conductivity considerably. The hazardous range of electric

conductivities is illustrated by the following numerical example.

### SAMPLE CALCULATIONS

A transfer line 8 ft. long, 4" i.d. is transferring LOX at a rate of 200 gpm.

$$\mu = .002 \text{ poise (* - liquid viscosity.)}$$

$$\rho = 1.2 \text{ gm/cm}^3 \text{ (* - liquid density.)}$$

$$D = 4 \times 2.54 = 10.2 \text{ cm - pipe diameter}$$

$$NRe = \frac{DU\rho}{\mu} = 8.5 \times 10^5$$

$$\therefore f = 0.004 (**).$$

$$E = 1.5$$

$$Z \sim 0.1 \text{ volt; estimated from ***.}$$

$$i_s = \frac{1}{2} f NRe \pi E E_0 U Z = 1.23 \times 10^{-8} \text{ amp}$$

$$T = \frac{E E_0}{k} = \frac{1.33 \times 10^{-13}}{k} \text{ sec}$$

$$V_s = \frac{i_s}{A k} = \frac{3.46 \times 10^{-2}}{k} \text{ volt}$$

$$E = \frac{1}{2} \frac{E E_0}{A} \frac{i^2}{k^2} = \frac{2.83 \times 10^{-29}}{k^2} \text{ m. j.}$$

\* Reference 28

\*\*Reference 24

\*\*\*Reference 15

TABLE D-I  
EFFECT OF ELECTRIC CONDUCTIVITY  
OF FLUID ON IGNITION HAZARD

k	T	V <sub>s</sub>	E
Electric Conductivity mho/cm. mho/cm.	Relaxation Time sec	Streaming Potential volts	Energy of Discharge m. j.
10 <sup>-10</sup>	.00135	346	.283 x 10 <sup>-5</sup>
10 <sup>-11</sup>	.0133	3460	.283 x 10 <sup>-3</sup>
10 <sup>-12</sup>	.133	34600	.0283
10 <sup>-13</sup>	1.33	3.46 x 10 <sup>5</sup>	2.83
10 <sup>-14</sup>	13.3	3.46 x 10 <sup>6</sup>	283
10 <sup>-15</sup>	133	3.46 x 10 <sup>7</sup>	2.83 x 10 <sup>4</sup>
10 <sup>-16</sup>	1330	3.46 x 10 <sup>8</sup>	2.83 x 10 <sup>6</sup>

Table D-I shows the effect of the electric conductivity of the fluid in the transfer system example, on the relaxation time (which can be considered as a criterion of charge leakage), on the streaming potential and energy of discharge. The hazardous range of conductivities is 10<sup>-11</sup> - 10<sup>-15</sup> mho/cm. At lower conductivities the relations used for the calculations do not apply as the number of charged particles, available in the system, is not sufficient to generate the large charge indicated by the equations.

#### EFFECT OF IMPURITIES

In a poor conducting fluid, the charge carrying particles are the small amounts of polar impurities present in the liquid. Solid impurities have an additional effect of generating static charges at their surfaces if they

are moving at a different velocity than the fluid. The magnitude of the hazard depends also on the nature of the impurity as a combustible impurity in LOX can, by igniting, initiate a greater explosion than the electrical discharge by itself.

A useful criterion for the ignition hazard would be the electrical conductivity of LOX. If more than one impurity is present, one impurity can enhance or defeat the effect of another (15). Data are not available for the electrical conductivity of pure or impure LOX. Since pure LOX does not generate a static charge (1, 20) it can be assumed that its conductivity is smaller than  $10^{-15}$  mho/cm.

An addition of a non-combustible, soluble, polar impurity at a concentration of a few ppm may increase the conductivity of LOX to over  $10^{-11}$  mho/cm where the rate of leakage of the charge is higher than the rate of generation. Such impurities will have to have low melting points, some solubility in LOX and high polarity. NO<sub>2</sub> or SO<sub>3</sub> may serve in this capacity.

#### EXPERIMENTAL WORK

Ebert and Hoffman (7) in a series of very careful experiments back in 1960 showed that pure liquid air does not generate a static charge. When large amounts of solid O<sub>2</sub> were added to the liquid air, no charge was generated. Small amounts of ice caused a considerable negative charge generation by movement of the ice on the liquid surface. The ice itself became positively charged.

Work done in the National Bureau of Standards in 1960 (20) showed that flow of pure liquid oxygen does not generate electrical charge and that very small amounts of moisture in the LOX generated considerable voltages. Solid particle contaminants generated voltages of order of many kilovolts.

Work done by Air Products also showed that pure liquid oxygen does not generate any charge. LOX containing 2-3 ppm CO<sub>2</sub> did not generate any charge. LOX containing 200-300 ppm CO<sub>2</sub> generated 3000 volts in 3 hours. This may have been due to some contamination with water. In most cases a negative charge was observed in the LOX. In some cases a positive charge was observed. The exact nature of impurity causing this effect was not established. Heating or cooling the coil in which the charge was generated did not effect the rate of charge generation.

### CONCLUSIONS

1. Pure liquid oxygen does not generate an electrostatic charge.
2. Solid and dissolved impurities, particularly water, in the LOX cause an electrostatic charge generation.
3. The hazardous range of impurity concentration is defined by electrical conductivity of LOX of  $10^{-11}$  -  $10^{-15}$  mho/cm.
4. The charge build up increases with velocity and with decreased diameter of the transfer line.

### RECOMMENDED PREVENTIVE MEASURES

1. Ground all metal tanks and lines.
2. Maintain LOX free of solid impurities and contamination with water.
3. Use large diameter lines and low velocities.
4. Monitor the electric conductivity of the LOX.
5. Increase the conductivity of LOX above  $10^{-11}$  mho/cm.

## APPENDIX E

### CRYOGENIC LIQUID BATCH SAMPLERS

#### OPERATING TECHNIQUES

AIR PRODUCTS AND CHEMICALS, INC.

MODEL A3A

#### PRINCIPLE OF OPERATION

The sampler is based on the common principle of trapping a known volume of a cryogenic liquid within a high-pressure container and allowing the liquid to vaporize to a high-pressure gaseous sample by normal heat leak. In the acquiring of a sample the liquid to be vaporized to the high-pressure gas sample is contained in the inner cup. (See Figure E-1) By proper manipulation of the valves, the entire container is filled with the liquid being sampled. There is, therefore, a protective liquid blanket surrounding the sample liquid in the inner cup, which prevents vaporization or fractionation of the trapped liquid. This surrounding liquid blanket is removed at a rapid rate (approximately 30 seconds duration) and the inner sample vaporizes as stated above. This method of insulating the trapped liquid by identical cold liquid is one of the unique features of this sampler (proprietary development - patent protection anticipated) and allows it to obtain a more representative sample than would be obtained by other "trapped liquid-vaporization techniques."

#### SPECIFICATIONS

Casing size - 25" x 12" x 8-3/4"

Weight - 30 pounds (including case)

Pressure Limits - Full vacuum to 2000 psig.

Pressure Gauge - 0 to 2000 psig.

Pressure Cylinder - Type 304 Stainless Steel seamless pipe. Walls 0.237" thick. Pressure cylinder rated at 3000 psig. Each valve equipped with an 1800 psig rupture disc. Valve seats and seals made of Kel-F.

Valves - Brass.

Liquid Sample Size - 17.0 cubic inches.

Cylinder Displacement - Approximately 150 cubic inches.

Gaseous Volume (Oxygen) - 14,500 cubic inches at standard conditions.

Final Sample Pressure (Oxygen) - 1300 psig.

#### SAMPLING INSTRUCTIONS

The sampling instructions are contained within the lid of the sampler carrying case and are reproduced here as Figure E-2.

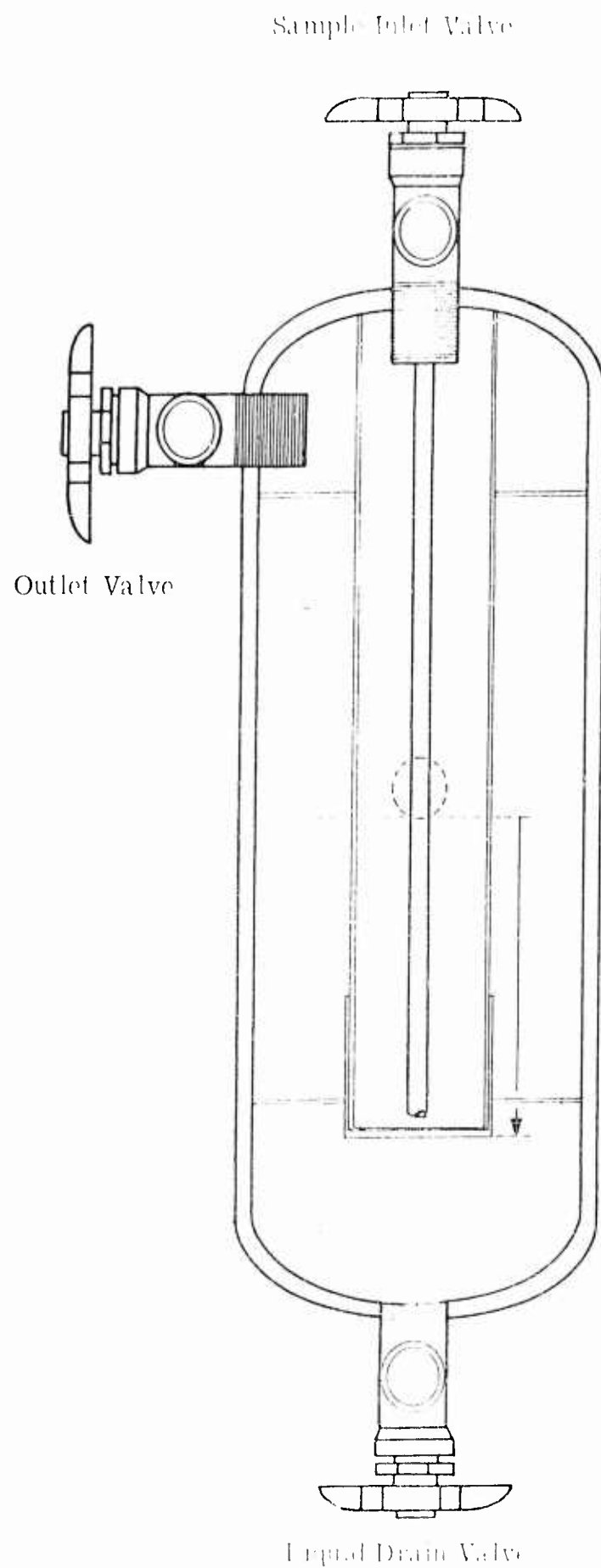
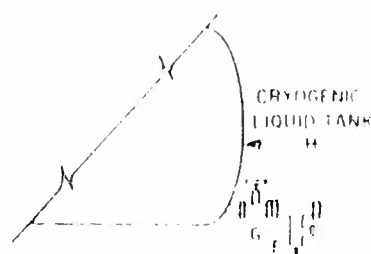
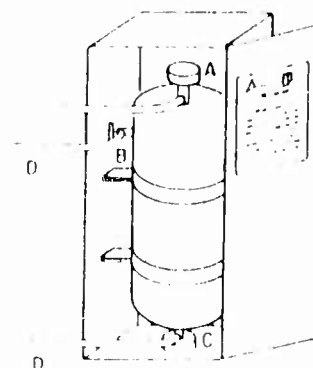


Figure E-1. Cryogenic Liquid Batch Sampler  
Air Products and Chemicals, Inc.



CRYOGENIC LIQUID  
BATCH SAMPLER  
MODEL A-3-A



SAMPLE INSTRUCTIONS

1. Place Opened Container in Upright Position as in the Above Sketch.  
DO NOT BLEED THE PRESSURE FROM SAMPLE CYLINDER.
2. Attach the Copper Tube Liquid Deflectors (D) to Valves (B) & (C). Tighten the Deflectors so that they Point Overboard on the Left Hand Side of the Container.
3. Using Appropriate Adapters Connect the Sample Line Between Bleed Valve (F) & Sample Valve (A).  
CAUTION: NEVER ATTEMPT TO SAMPLE A TANK OR SYSTEM WHICH HAS NOT HAD A BLEED VALVE (F) ATTACHED TO THE SAMPLE VALVE (G).
4. Tighten All Sample Line Connections and Slowly Open Valve (A) Allowing the Sample Line to be Purged through Valve (F).
5. When 75 % of the Pressure in the Sampler has been Depleted, Close Valve (F).
6. Purge Valves (B) & (C) by Alternately Opening and Closing these Valves until the Remaining Pressure is Depleted. Valves (B) & (C) should be Closed At the End of this Operation.
7. Open Valve (G). Open Valve (B). Valve (A) Should be Open from Step 4, the Sampler will Begin to Fill with Liquid.
8. If Possible at this Time, Pressurize Cryogenic Liquid Tank to Approximately 10-15 PSIG.
9. When Liquid Starts to Flow From the Deflector on Valve (B) and It is Felt a Representative Sample has been Obtained, Perform the Following Valve Manipulations in Quick Succession.
  - a. Close Valve (B)
  - b. Close Valve (A)
  - c. Open Valve (C)
10. When Liquid Ceases to Flow from the Deflector on Valve (C) - (Gas Should Still Be Escaping), Close Valve (C).
11. Using Proper Precautions to Prevent Being "Burned" by Cold Piping Open Valve (F) and Immediately Close Valve (G).
12. Disconnect the Sample Line at Valve (A) and Lay the Sampler Container Flat (Lid Side Up for 20" min.).
13. On Warning to be Ignored, when the Sample Gauge Should Indicate a Pressure of 40-50 PSIG.
14. The Copper Tube Liquid Deflectors (D) can be Removed and Replaced in the Sampler.

## COSMODYNE CORPORATION

### MODEL CS44

#### PRINCIPLE OF OPERATION

The Cosmodyne Cryogenic Sampler operates on the shielded cup principle - that is, the liquid itself is used to cool a shielding space and sampling cup prior to the introduction of fresh liquid to the sampling cup. Figure E-3 is a schematic of the sampler's arrangement. It consists of two cups located inside a pressure vessel with inlet, outlet and sampling valve located as shown. Accurate sampling requires the inner-most cup to be precooled. This is done by allowing liquid to flow in the inlet port and between the shielding cup and sampling cup with the sampling valve closed so that no liquid enters the sampling cup. After the sampling cup is adequately cooled, the sampling valve is opened to admit liquid into the cup. When the valve is reclosed, the liquid is trapped in the sampler and will vaporize as a result of atmospheric heating. Once the sample is trapped the flow of liquid is shut off. Under ordinary conditions (70°F environment), the sample will completely vaporize without additional heating in approximately fifteen minutes.

After the liquid becomes a gas, it can be analyzed by any one of several conventional laboratory instruments.

#### SPECIFICATIONS

Casing Size - 8" x 8" x 17 1/4"  
Weight - 20 lbs  
Final Sample Pressure - 500 psig  
Material - Stainless Steel  
Volume of Cylinder - 4.4 liters

#### SAMPLING PROCEDURE

1. Pressurize liquid tank as desired.
2. Remove top of carrying case
3. Remove inlet and outlet caps
4. Connect 1/2" fill line from liquid tank to sampler inlet.
5. Open liquid tank outlet valve

6. Allow sampler to cool until steady flow of liquid appears.
7. Open sampling valve by turning handle at top of sampler until it stops.
8. Close sampling valve.
9. Close liquid tank outlet valve.
10. Disconnect fill line.
11. Replace inlet and outlet caps.
12. Replace top of carrying case.

#### SAFETY PRECAUTIONS IN SAMPLER USE

Normal rules involving the safe handling of cryogenic liquids and/or oxidants should be applied in the use of this sampler. Specific rules for safe operation are listed below:

1. In sampling cryogenic liquids, protect the body from contact with the liquid or cold piping by using acceptable, approved gloves, a hood and a hard hat, if necessary. If protection is not provided for the face and eyes with a hood, a transparent face shield should be worn.
2. The major hazard involved in the use of this sampler is the possibility of the operator inadvertently trapping cold liquid in a closed section of piping. This possibility is protected against by the use of safety discs in the sampler itself. However, extreme care and caution should be exercised in the handling and manipulation of the sample line and associated piping to prevent trapping liquid in a closed line between the sampler and the sampled tank. Before closing any valve between the sampler and the sampled tank, the operator should assure himself that liquid will not be trapped.
3. Normal care concerning smoking, open flames, static charges, etc. should be exercised when sampling liquid oxygen. Special care should be exercised after the operator has been in prolonged contact with oxygen vapor to assure that his clothing is well purged before exposing himself to an area where open flames, static charges, smoking, etc. might be prevalent.

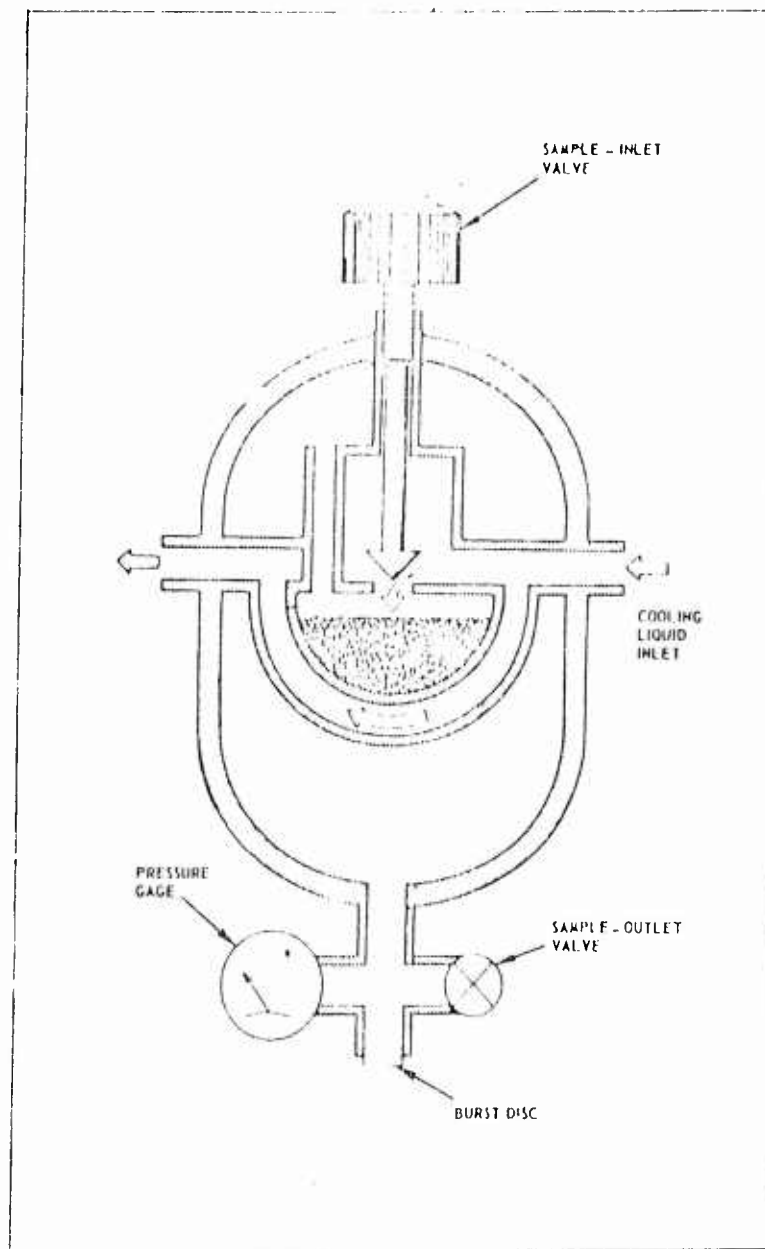


Figure E-3. Cryogenic Gas Sampler  
Cosmodyne Corporation

## APPENDIX F

### ACETYLENE SPOT-CHECKING PROCEDURE

#### 1. ANALYSIS

The acetylene content of the liquid oxygen is determined from the color intensity produced by a chemical reaction with the acetylene.

#### 2. PRINCIPLE OF OPERATION

The liquid oxygen sample is poured into a tube which contains a small amount of silica gel and which is held at liquid nitrogen temperature. The gel and the liquid are well mixed, the sample is decanted and the gel is immersed in a small amount of acetylene test solution. The acetylene reacts with the solution to form the red, copper acetylide, complex.

#### 3. TEST EQUIPMENT

The test equipment consists of a 1 quart sample collection dewar flask, a 1/2 pint wide-mouthed dewar flask, a rack for test tubes, a test tube clamp, a glass stirring rod, a dropping bottle, a reagent bottle, six test tubes, color standards, chemicals, and silica gel.

- a. Dewar Flask. A one-quart Dewar flask (1) is used to obtain and hold a liquid oxygen sample.
- b. Test Tube Rack. A test tube rack (2) for holding the test tubes is included. Store the tubes in the carrying kit.
- c. Test Tube Clamp. A wire hand clamp (3) holds the cold test tube to prevent liquid oxygen burns.
- d. Test Tubes. There are six six-inch pyrex tubes (4) calibrated at the 3 ml and 20 ml levels.
- e. Dropping Bottle. This bottle (5) is used to add drops of the hydroxylamine hydrochloride to the test tube.
- f. Wide-Mouthed Dewar Flask. The test tube sample is supported in this 1/2 pint flask (6) by the test tube clamp during the test. It contains the liquid nitrogen used in sub-cooling the sample.
- g. Carrying Kit. The wooden or metal kit (7) is fabricated for convenient carrying of the testing apparatus.

- h. Test Solution Addition Bottle. This bottle is used for simple and accurate reagent addition (8).
- i. Color Standards and Comparator Rack. (9)
- j. Glass Stirring Rod. The glass stirring rod (10) is used to mix the liquid oxygen sample with the silica gel.

#### 4. ACETYLENE TEST SOLUTION

Prepare the test solution as follows:

- Step 1. Add one gram of soluble starch to 10 ml of distilled water and stir to form a thin paste. Pour paste into 200 ml of boiling distilled water and stir. Allow to cool.
- Step 2. Dissolve 5 grams of copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in a one liter volumetric flask.
- Step 3. Add 50 ml concentrated ammonium hydroxide (Specific Gravity at  $60^\circ/60^\circ\text{F} = 0.900$ ; Assay 28.4%  $\text{NH}_3$ ) to the copper sulfate solution.
- Step 4. Add the starch solution prepared in Step 1 to the copper ammonia solution and dilute to the one liter mark with distilled water. Store in the test solution addition bottle (8).

NOTE: This acetylene test solution has a deep blue coloration.

#### 5. HYDROXYLAMINE HYDROCHLORIDE SOLUTION

Dissolve 36.0 grams of hydroxylamine hydrochloride in 100 ml of distilled water and store in the 4 oz. polyethylene dropping bottle (5).

#### 6. TEST PROCEDURE

Purge the sample line before procuring a liquid oxygen sample.

Precool the one quart Dewar flask by filling it with liquid oxygen from the sample line. Allow to stand about one minute. Discard contents of Dewar and refill from sample line.

Use a clean, dry 150 mm by 20 mm Pyrex test tube calibrated at the 3 ml and 20 ml levels to perform the test.

Add 1/4 ml (0.3 grams) of the silica gel powder to the test tube, and slowly immerse the test tube into the wide-mouthed dewar which has previously been filled with liquid nitrogen. Using the test tube clamp as a "rest" on the edge of the dewar, support the test tube in an upright position so that the level of liquid nitrogen is at or slightly above the 20 ml mark on the tube. Pour the liquid oxygen sample from the sample collection dewar into the subcooled test tube to the 20 ml mark.

Slowly immerse the glass stirring rod into the liquid nitrogen in the dewar until it is cooled. Remove the stirring rod and immerse it in the liquid oxygen sample in the test tube and stir for one and one half to two minutes. In stirring attempt to bring all of the liquid in the tube in contact with the gel.

After stirring the required time, remove the stirring rod from the tube and allow the gel to settle to the bottom (approx. 5 seconds). Remove the sample tube from the liquid nitrogen bath and pour out (decant) all of the liquid oxygen, being careful to keep the gel in the bottom of the tube. As quickly as possible, add the acetylene test solution from the test solution addition bottle to the 3 ml mark.

When the solution has warmed to ambient conditions, add exactly 12 drops of the hydroxylamine hydrochloride solution, and allow the test tube to stand for 15 minutes for full color development.

The appearance of any pink or red color indicates the presence of acetylene. Compare any color developed with the standards to determine the acetylene concentration.

## 7. PREPARATION OF COLOR STANDARDS

1.0 Molar PPM Color Standard - Add 2.0 ml concentrated hydro-

chloric acid (Specific Gravity at 60°/60° F = 1.191; Assay 37.7% HCl) to 150 ml distilled water in a beaker and stir. Add the following accurately weighed quantities of Cobaltous Chloride, Hexahydrate; Cupric Sulfate, Pentahydrate; and Ferric Chloride, Hexahydrate to the beaker.

CoCl <sub>2</sub> · 6H <sub>2</sub> O	-	10.00 gms
CuSO <sub>4</sub> · 5H <sub>2</sub> O	-	2.00 gms
FeCl <sub>3</sub> · 6H <sub>2</sub> O	-	0.30 gms

Stir until dissolved and quantitatively transfer to a 200 ml volumetric flask. Dilute to the mark with distilled water and shake well.

Add about 15 ml of this solution to a 150 mm by 20 mm Pyrex Test Tube and seal. The color and color intensity when viewed from the side of the tube against a white background is essentially equivalent to that produced by liquid oxygen containing 1 ppm acetylene when tested in accordance with the above procedure.

0.25 Molar PPM Color Standard - Add 2.0 ml concentrated hydrochloric acid (Specific Gravity at 60°/60° F = 1.191; Assay 37.7% HCl) to 150 ml distilled water in a beaker and stir. Add the following accurately weighed quantities of Cobaltous Chloride, Hexahydrate; Cupric Sulfate, Pentahydrate; and Ferric Chloride, Hexahydrate to the beaker.

CoCl <sub>2</sub> · 6H <sub>2</sub> O	1.90 gms
CuSO <sub>4</sub> · 5H <sub>2</sub> O	1.30 gms
FeCl <sub>3</sub> · 6H <sub>2</sub> O	0.20 gms

Stir until dissolved and quantitatively transfer to a 200 ml volumetric flask. Dilute to the mark with distilled water and shake well.

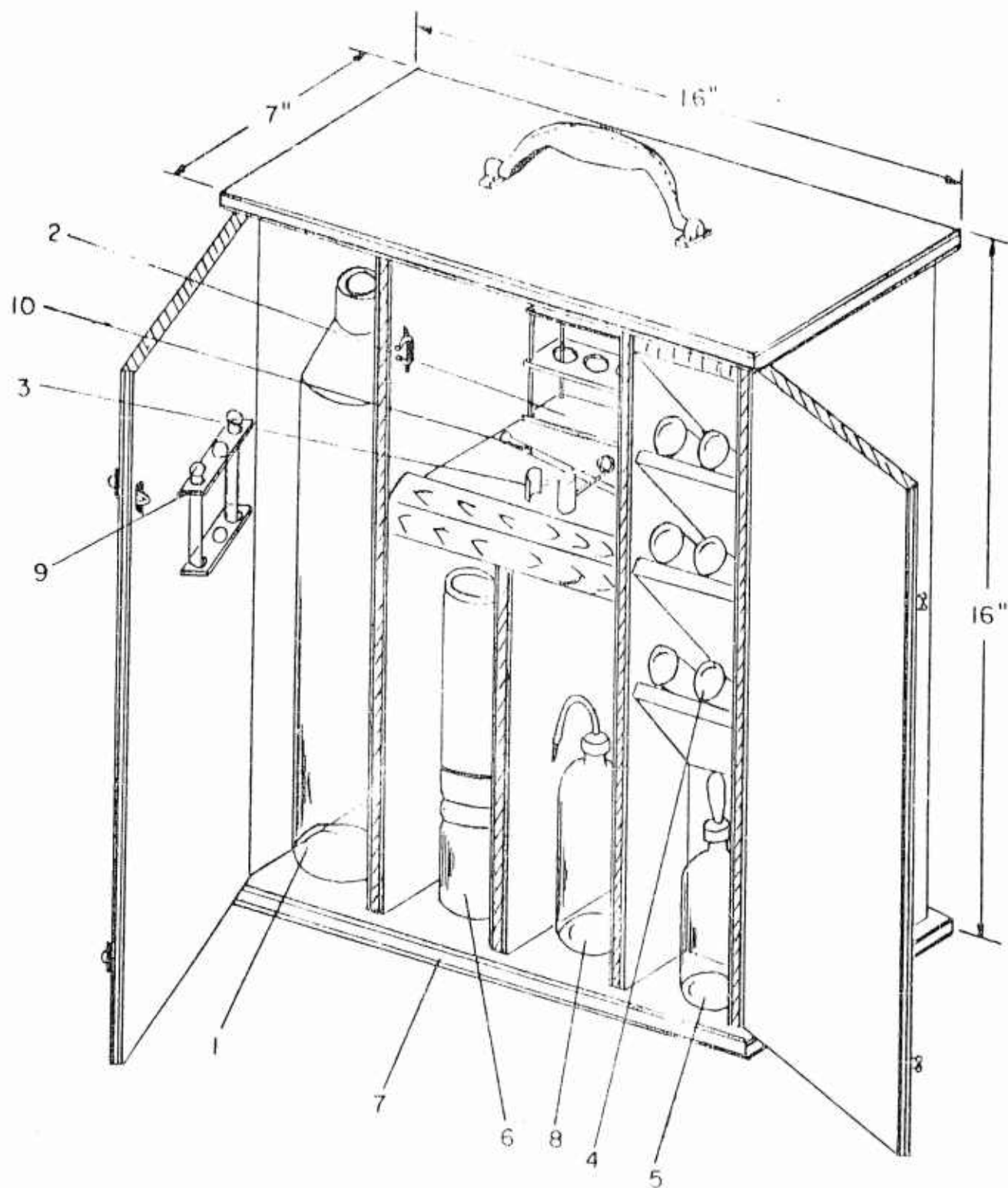
Add about 15 ml of this solution to a 150 mm by 20 mm Pyrex Test Tube and seal. The color and color intensity when viewed from the side of the tube against a white background is essentially equivalent to that produced by liquid oxygen containing 0.25 ppm acetylene when tested in accordance with the above procedure.

8. SPARE PARTS

Spare parts, spare parts lists, and prices are available from the Spare Parts Department.

9. ADDITIONAL COLOR STANDARDS

Sealed tubes of color standards equaling 0.1, 0.25, and 0.50 ppm acetylene by weight for use in compliance with Air Force propellant oxygen and nitrogen specifications are available from the Spare Parts Department of Air Products, Incorporated. The 1.0 ppm and 0.25 ppm color standards described in paragraph seven (7) above are prepared as molar concentrations.



- |                                     |                              |   |
|-------------------------------------|------------------------------|---|
| 1. Sample Collection<br>Dewar Flask | 4. Test Tubes                | 7. Carrying Kit                               |
| 2. Test Tube Rack                   | 5. Dropping Bottle           | 8. Reagent Bottle (Test<br>solution addition) |
| 3. Test Tube Clamp                  | 6. Wide Mouth Dewar<br>Flask | 9. Color Standards &<br>Comparator Rack       |
|                                     |                              | 10. Stirring Rod (Glass)                      |

Figure E-3. Acetylene Analytical Apparatus

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